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JRC

Institute for Transuranium Elements



ANNUAL REPORT 2006



The mission of ITU is to provide the scientific foundation for the protection of the European citizen against risks associated with the handling and storage of highly radioactive elements.

ITU's prime objectives are to serve as a reference centre for basic actinide research, to contribute to an effective safety and safeguards system for the nuclear fuel cycle, and to study technological and medical applications of transuranium elements.

European Commission

Joint Research Centre

This report was compiled and edited by
J. F. Babelot, T. Fanghänel, J. Magill, G. Weber

Inquiries for more details should be addressed to
Jean-François Babelot, Programme Office,
Institute for Transuranium Elements
P.O. Box 2340, 76125 Karlsruhe
Tel.: +49 (0) 7247-951 437
Fax: +49 (0) 7247-951 591
E-mail: jean-francois.babelot@ec.europa.eu

This publication and more information on the
Institute may be found on the Internet:
<http://www.jrc.ec.europa.eu> and <http://itu.jrc.ec.europa.eu>

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The Institute for Transuranium Elements is one of the seven institutes of the European Commission's Joint Research Centre, located in Karlsruhe, Germany. It is our mission to provide the scientific foundation for the protection of the European citizen against risks associated with the handling and storage of highly radioactive elements.

Research is focused on:

- Basic actinide science
- Safety and safeguards systems for the nuclear fuel cycle, and
- Technological and medical applications of transuranium elements

Many new scientific results have been obtained in 2006 only a few of which can be highlighted in this report. Considerable progress was made in understanding the nature of the magnetic and non-magnetic correlations in strongly correlated electron systems of actinides. The new 7th edition of the Karlsruhe Nuclide Chart, now mandated to ITU, was published. The fabrication and characterisation of two Molybdenum based composite nuclear fuels to be irradiated in the Phénix reactor in France, was successfully completed. The experiment will provide essential data concerning the behaviour under irradiation of these advanced fuels. Pyro-partitioning of actinides from fission products has been demonstrated by applying the technique to a high-level liquid waste from reprocessing of spent nuclear fuel. Regarding the safety of waste disposal, unequivocal evidence that the macroscopic properties and microstructure alterations associated with accumulating radiation damage in solid wasteform are not dependent on the rate of deposition of the decay dose was obtained.

ITU secured a seat on the steering committee of the international NFIR (Nuclear Fuel Industry Research Program) project. The project investigates the high burn-up properties of uranium oxide and MOX fuel and the role of the high burn-up structure on fuel disruption during a reactor power transient. Further progress was the inclusion, in the TRANSURANUS fuel performance code, of a model for hydrogen absorption by the cladding of a VVER (Russian-type reactor) during a loss-of-coolant accident. The application of alpha emitters for cancer therapy and the treatment of infectious diseases was further developed. The operation of DG-TREN's on-site laboratories at the site of the two large European reprocessing plants in Sellafield (UK) and La Hague (F) continued, taking into account the new safeguards strategy of DG-TREN.

Training courses on "response to illicit trafficking of nuclear materials" were jointly organised with the IAEA and held at ITU. Upon Member State request, samples of seized nuclear material were subjected to nuclear forensic investigations at ITU.

Celebrating the 25th anniversary of our collaboration with IAEA was one of the institute's highlights in 2006. This event underlined our activities in the field of safeguards und combating illicit trafficking.

Our prominent visitors included Janez Potočnik, Commissioner for Science and Research and Heinz Fenrich, Lord Major of the city of Karlsruhe.

2006 was a year of changes in the management of ITU. At the beginning of the year Jean-Pierre Michel was appointed as acting director after Gerard Lander, the former director of ITU, stepped into retirement at the end of 2005. Since June 2006 I have the honour to be the new director of ITU. I wish to thank Jean-Pierre Michel for his excellent job as acting director.

I would like to express many thanks to our numerous research partners, visitors, customers and collaborators, including the necessary administrative support. We are also very grateful to the Scientific Advisory Group – W. Sandtner, U. Blohm-Hieber, J. Bouchard, D. Clark, F. Karlsson, J. M. Martinez Val, A. Seibold, W.G. Stirling – whose advice we tried to make reality in 2006. Last, but not least, many thanks to the staff of ITU for performing excellent research.



*Director
Thomas Fanghänel*

Spent Fuel Management

The safe disposal of highly active waste and spent nuclear fuel dominates the nuclear debate in several countries. Approximately 45000 tons of spent nuclear fuel is presently in interim storage in the European Union. The two approaches for spent nuclear fuel management favoured by the Member States consist of intermediate storage with subsequent conditioning for final disposal, and intermediate storage with subsequent reprocessing (partitioning) for lowering the radiotoxicity (transmutation) before final disposal in geological formations.

- The work performed at ITU aims at discerning the mechanisms of leaching of irradiated uranium oxide and MOX fuel in water by measuring the fuel corrosion rate under controlled chemical conditions, and studying the solid state physical-chemical properties of irradiated fuel.
- The objective of the research on partitioning and transmutation is to efficiently separate the long-lived nuclides from the waste, to develop the technologies to allow their incorporation in well-designed fuels or targets, and to transmute them in dedicated reactors by neutron capture or fission into nuclides with much shorter half-lives.

Safety of Nuclear Fuel

The safety of nuclear installations remains a major public concern even if energy production by nuclear fission is considered a mature technology. Licensing authorities request safety improvements and industry tries to increase operational efficiency. The objective of ITU is to contribute to nuclear safety improvements by studying in detail phenomena that occur in light water reactor fuel rods at extended times of operation.

Furthermore, the understanding of the behaviour of nuclear fuel under incident and accident conditions allows improvement of the response and precautions to be taken if such events occur.

Safeguards R&D

Stopping the further spread of nuclear weapons is a major policy objective of the European Union. The inspection authorities, DG TREN (Transport and Energy) of the European Commission and the International Atomic Energy Agency, are charged with the implementation of safeguards measures to control the use of nuclear materials within the European Union and worldwide. The Institute is a long-standing partner of the Safeguards Inspectorates provid-

ing assistance and expertise particularly relevant to plutonium handling facilities, such as reprocessing and MOX fuel fabrication plants. For more than 3 decades, ITU has been providing new analytical and characterisation tools.

Radioactivity in the Environment

The protection of citizen and environment against ionizing radiation requires accurate and precise analytical methods for the detection and quantification of radionuclides in the different ecosystems. Moreover, there is a stringent need for the independent verification of radioactive releases into the environment.

The JRC competence in trace detection and analysis is used to develop projects and co-operation for the surveillance of radioactivity in the environment, including studies on migration patterns of actinides in the biosphere and assistance in radiological emergencies.

Basic Actinide Research

A good knowledge of fundamental physical, chemical and material science data on actinides and actinide-containing products is a pre-requisite for solving of any technological problems or improvement processes. Basic actinide research aims at advancing the basic knowledge necessary in support to EU policies dealing with nuclear fuels, nuclear waste or nuclear safeguards.

Through its various training programmes, such as the Actinide User Lab and Summer School, ITU welcomes young professionals needed to keep the fission option open and to maintain a high level of scientific competence.

Alpha-Immunotherapy and Cell Toxicity

Cancer continues to be one of the major preoccupations of the European citizen and one of the great challenges for research. ITU promotes, in cooperation with university hospitals, the development of a cancer therapy based on the use of alpha-particle emitting nuclides. Their effect on healthy cells is minimal due to high linear energy transfer values of the alpha particles which deposit their energy over a few cell diameters only. The objective of ITU is to make its facilities and expertise in handling highly radioactive alpha-nuclides available to develop, test, validate and optimise a drug against different types of cancers, consisting of a suitable alpha-emitter, a cancer specific carrier (antibody, peptide, etc.) and a chelator (combining nuclide and carrier).

Events



V. Rondinella describes the Spent Fuel Characterisation project to MP S. Kotting-Uhl

Visit of Mrs. Sylvia Kotting-Uhl, (Bündnis 90/DIE GRÜNEN Party)

February • MP Sylvia Kotting-Uhl, also current spokesperson for environmental questions of the German parliamentary party "Bündnis 90/Die Grünen" paid a visit to the ITU. She wished to acquire information on the work performed at the institute. A guided tour of the laboratories included the projects Alpha-Immunotherapy, Spent Fuel Characterisation and Radioactivity in the Environment.

7th Training Course on Radioactivity, Radionuclides, & Radiation with Nuclides.net

April • The 7th nuclear science training course on Radioactivity - Radionuclides - Radiation with Nuclides.net, organized by ITU was held in Karlsruhe 26th to 28th April, whereas the 8th training course took place at the Nuclear Training Centre of the Jozef Stephan Institute in Ljubljana, Slovenia, from 13th to 16th September. The three-day courses covered a wide range of topics in the field of nuclear science and technology. The courses emphasized interactive and hands-on learning through the use of the ITU software package Nuclides.net. Special lectures were held on isotope paleoclimatology and radioactive dating methods. A total of seventy participants, around half of them women, from new EU Member States and Candidate Countries, South Korea, Switzerland and the Ukraine attended the courses.



Nuclides.net training course session

7th EMAS Regional Workshop on Electron Probe Microanalysis of Materials Today - Practical Aspects

May • The EMAS Regional Workshop is a biennial event designed to provide postgraduate students, researchers and technicians in materials science and engineering with basic knowledge of the capabilities and limitations of electron probe X-ray microanalysis (EPMA). The workshop was arranged as a low-cost meeting with lectures on practical and theoretical aspects of EPMA given by internationally recognised experts. The core topics of the 7th EMAS Regional Workshop were electron beam - specimen interactions, basic Monte Carlo simulation, X-ray spectroscopy, sample preparation, quantitative electron probe microanalysis of light elements and thin film analysis.



The participants of the 7th European Microbeam Analysis Society (EMAS) Regional Workshop in front of the Karlsruhe castle



New ITU Director

June • On 1st June Prof. Dr. Thomas Fanghänel took up his duty as ITU Director with a welcome party. With a back-

ground in Chemistry (Diplomchemiker), a Ph.D and Habilitation in Inorganic and Physical Chemistry from the Technical University Bergakademie Freiberg, he is Professor of Radiochemistry at the Ruprecht-Karls-University Heidelberg. Before his appointment as Director of ITU, he was head of the Institute for Nuclear Waste Disposal (INE) of the Forschungszentrum Karlsruhe, after having been Director of the Institute of Radiochemistry, Forschungszentrum Rossendorf and Professor of Radiochemistry at the University of Dresden. He has more than 20 years of research experience with special expertise in actinide chemistry and long-term safety aspects of nuclear waste disposal. Since 2003 he is member of the Reactor Safety Commission of the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety.

11th International Technical Working Group (ITWG) Annual Meeting

September • The Nuclear Smuggling International Technical Working Group (ITWG) held its 11th meeting from 26th to 29th September in Speyer. The meeting was organised by ITU (ITU is co-chairing the ITWG, together with Lawrence Livermore National Laboratory), it was attended by more than 50 participants from the G-8 countries, EU Member States, IAEA, Europol, Australia, Tajikistan, Brazil among others. Prior to the meeting a visit to the ITU laboratories was arranged, with special attention to those laboratories involved in nuclear forensics. The first part of the meeting focused on scientific and operational issues in nuclear forensics, the second part addressed questions related to interagency and international collaboration. In a table-top exercise the participants discussed a scenario (with possible involvement of radiological material) and developed a response procedure.

Visit of CRIEPI's President (Japan)

Mr. Shirato and the Japanese delegation (Mr. Akita, Mr. Inoue, Mr. Hishina) paid a visit at ITU beginning of September. The collaborations between CRIEPI and

ITU were reviewed and potential agreements on future joint activities were discussed. In particular, the High Burn-up Rim Project (HBRP) was presented. The last developments in the field of safety of nuclear fuels and partitioning & transmutation were shown during a visit to the ITU laboratories.



Mr. Shirato signing the institute's "golden book"

Celebrating 25 Years of Co-operation between the European Commission and the International Atomic Energy Agency on Nuclear Safeguards

October • On 5th October, the 25th anniversary of the EC support programme to the IAEA was celebrated in Karlsruhe. The Joint Research Centre has been operating this support programme through R&D activities, which were used by the Department of Safeguards of the IAEA. The ceremony was attended by some 40 journalists from all over Europe.



Deputy Director General of the IAEA, Olli Heinonen, presenting the IAEA Certificate of Appreciation to JRC's Director General, Roland Schenkel and ITU's Director, Thomas Fanghänel

Presentations by JRC's Director General, Roland Schenkel and by the Deputy Director General of the IAEA, Olli Heinonen, emphasized the fruitful cooperation and the high standard, which nuclear material safeguards has achieved. A safeguards workshop

Events

was held the day prior to the official ceremony. During this workshop the R&D needs of the IAEA and the scientific/technical achievements (in response to the needs) were presented by high ranking IAEA officials and by JRC senior scientists.

Visit of the Commissioner Janez Potočník

October • On 25th October, the Commissioner for Science and Research, Janez Potočník, of the European Commission visited the Institute. On that occasion, a tour of the facilities was organised. The Alpha-Immunotherapy, Basic Actinides, Hot Cells and Safeguards laboratories were visited. The Commissioner was impressed with the presentations and with the enthusiasm of the researchers. In his address to the staff, he emphasized the role of ITU in protecting the citizen from the risks associated with the handling and storage of highly radioactive elements, and in making Europe cleaner, safer, more competitive.



Commissioner for Science and Research J. Potočník handling a piece of plutonium crystal in a glove box

80th JRC Board of Governors Meeting

November • On 23rd to 24th November, the 80th meeting of the JRC Board of Governors took place in Karlsruhe. Before starting their discussions, the participants visited the ITU laboratories.



JRC Board of Governors in front of the institute

Visit of the Lord Mayor of Karlsruhe

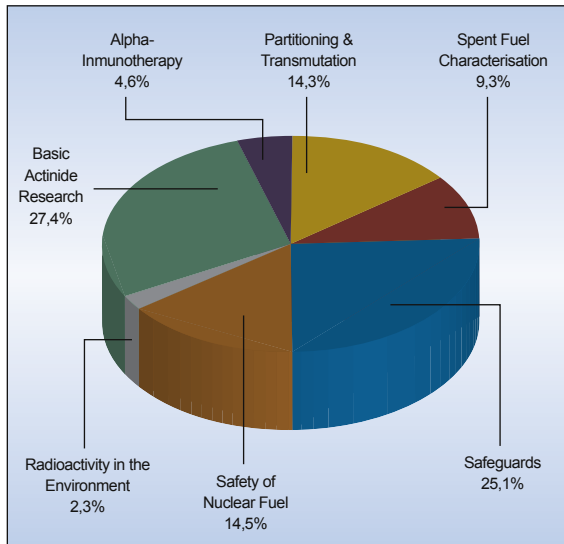
December • On 6th December, the Lord Mayor of Karlsruhe, Heinz Fenrich and the coordinator of the Technology Region Karlsruhe, J.G. Ehlgötz, visited ITU to get an insight into the installations of the Institute and its research programme. It was agreed to strengthen the collaboration between the city of Karlsruhe and ITU, in the frame of the programme "Technology Region".



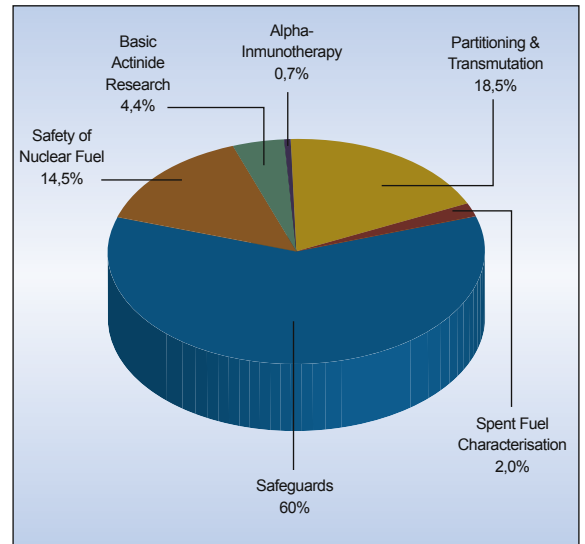
Visit of the ITU laboratories by H. Fenrich, Lord Mayor of Karlsruhe, and first attempt to work at the hot cells with telemanipulators

OVERVIEW

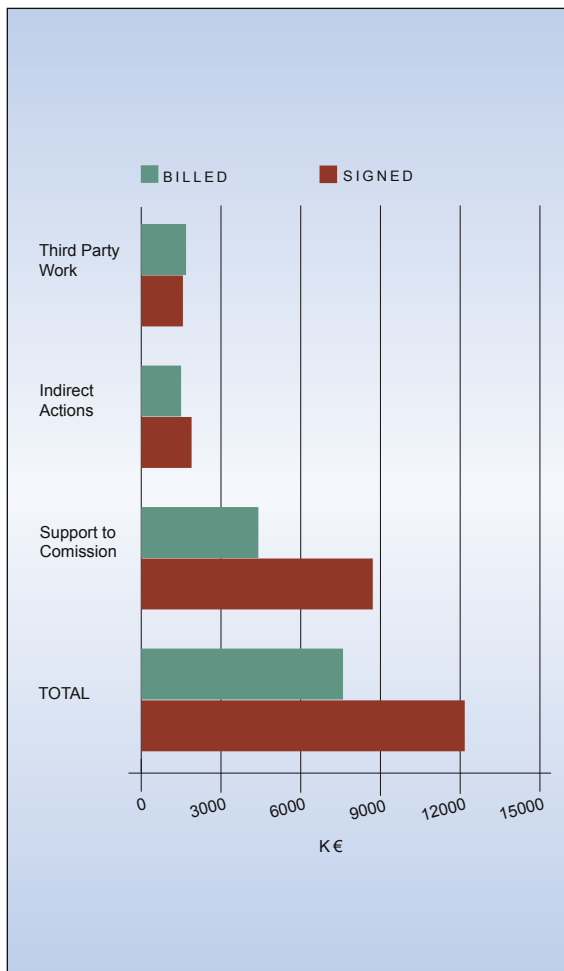
Facts & Figures



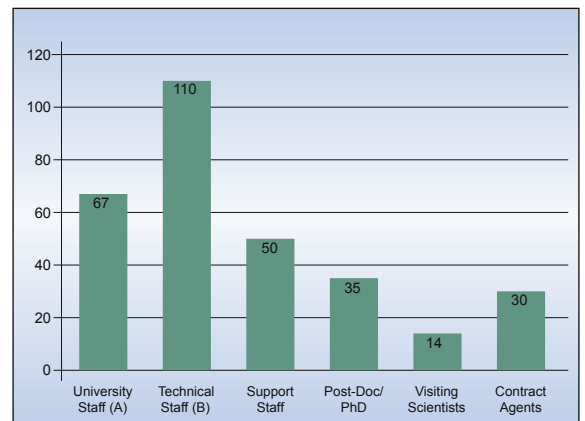
Institutional Budget Overall Volume 2006: 37,4 M€



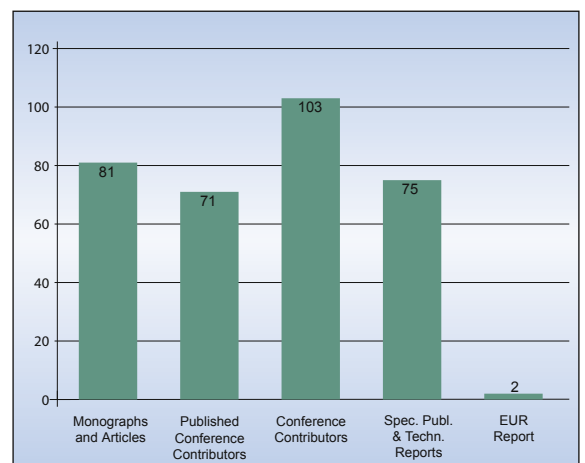
Competitive Budget Assigned to Institutional Activities Overall Volume 2006: 7,6 M€



Competitive Activities - Billed vs. Signed 2006



Distribution of the Staff at ITU (Dec. 2006)



Publications 2006

Organisation Chart



1. Safeguards Research and Development

Contributing to Nuclear Safeguards and Nuclear Security

Introduction

In 2006 issues related to nuclear safeguards, non-proliferation and nuclear security were high on the political agenda and attracted also considerable media attention. This was mainly due to the ongoing efforts in Iran for building up uranium enrichment capabilities and the poisoning of an individual using Po-210. Beyond the areas related to these spectacular events, attention needed to be attributed also to the traditional safeguards challenges like the verification of nuclear material in large reprocessing plants and in fuel fabrication plants.

The Institute for Transuranium Elements provided support to IAEA and to DG TREN through measurement services, consultancy, training and through dedicated research activities. The measurement services comprised the operation of the on-site laboratories at Sellafield and La Hague, the support of physical inventory verifications at fuel fabrication plants using mobile equipment and the analysis of samples taken by safeguards inspectors and shipped to ITU.

In addition to the safeguards activities, also the area of illicit trafficking of nuclear material and nuclear forensic analysis received significant attention. The Institute's involvement in international activities, in conceptual and methodological development, as well as the collaboration with national authorities in different Member States has constantly increased. In addition, the laboratory work aimed at broadening the scientific basis for nuclear forensic investigations was continued.

Celebrating 25 years of support to the International Atomic Energy Agency

The scientific and technical support to the Department of Safeguards of the International Atomic Energy Agency (IAEA) is organised through the „Member State Support Programme“. The European Commission's support to the IAEA started in 1981 and has been carried out by the Joint Research Centre and in particular by three institutes of the JRC which offered tailored expertise: the Institute for Transuranium Elements (ITU), the Institute for Reference Materials and Measurements (IRMM) and the Institute for Protection and Security of the Citizen (IPSC). On 4-5 October 2006, the 25th anniversary of the European Commission's Support Programme to the

IAEA was celebrated at the Institute for Transuranium Elements in Karlsruhe, Germany. In the official ceremony the history and the prospects of the EC support programme to the Department of Safeguards were described. The role of Nuclear Safeguards has evolved from the 'simple' verification of the correctness of a State's declaration, to the more complex challenge of ensuring that all nuclear related activities are properly described. In order to keep pace with changing challenges, the IAEA needs to apply the most advanced scientific and technical detection and verification tools. The IAEA's Deputy Director General, Olli Heinonen, emphasized in his speech the impact which the JRC's scientific developments had on the verification activities of the Department of Safeguards. ITU's contribution to the EC Support Programme has always focused on the analysis of samples of nuclear material. Recently, specifically developed measurement equipment was transferred to the IAEA's on-site laboratory at the reprocessing plant of Rokkashomura (Japan), the respective training was provided to IAEA staff and dedicated software is being developed. Moreover, an increasing number of samples of nuclear material are analysed in ITU. The measurements performed concern isotopic composition and chemical impurities. Such data provide useful information on the consistency of Member State declarations, especially under the Additional Protocol.

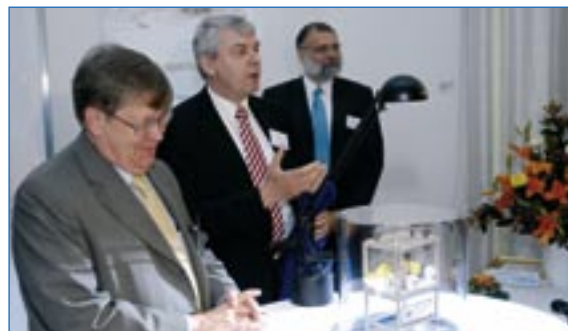


Fig. 1: The Director General of the JRC, Roland Schenkel, and the Director of ITU, Thomas Fanghänel, presenting a miniaturized glove-box to the Deputy Director General of the IAEA, Olli Heinonen, at the occasion of the 25th anniversary of the EC Support Programme to the IAEA

New COMPUCEA instrument for in-field accountancy verification measurements

For many years now, analysts from ITU have provided on-site analytical measurement support to Euratom and IAEA safeguards inspectors during their physical

inventory verification (PIV) campaigns in European Low-Enriched Uranium (LEU) fuel fabrication plants. The analytical measurements to be performed include the accurate determination of the uranium element content and ^{235}U enrichment in production samples (mostly pellets and powders) withdrawn by the Safeguards inspectors from the nuclear material inventory. The requested analyses are achieved with a measurement technique called COMPUCEA (Combined Procedure for Uranium Concentration and Enrichment Assay), which is based on the radiometric techniques of absorption edge spectrometry for the element assay, and on passive high-resolution gamma spectrometry for the ^{235}U abundance determination.

With the primary objective of producing a simplified instrumental variant better adapted to the requirements for in-field use, a 2nd generation of COMPUCEA for the uranium element assay has been developed at ITU [1]. The primary design goals were (i) to eliminate the radioactive sources needed in the 1st generation, and (ii) to make use of a radiation detector which does not require cooling with liquid nitrogen. Both goals have been met fully with the new COMPUCEA instrument shown in Fig. 2. In the new COMPUCEA the uranium concentration is determined from an X-ray absorption measurement across the LIII absorption edge of uranium (see Fig. 3). The instrument uses a miniaturized X-ray tube as photon source, and a Peltier-cooled Si detector for high-resolution spectrometry. Since high-accuracy absorption measurements are only possible on liquid samples, a prior sample dissolution is required

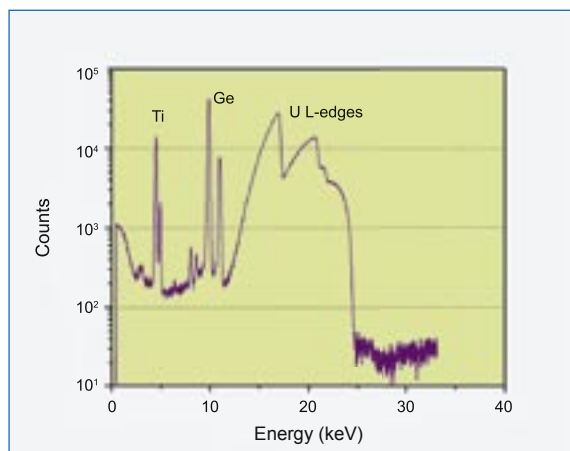


Fig. 3: Example of an L-edge absorption spectrum from a uranium sample (the Ti and Ge K-X rays are added on purpose for instrument control)

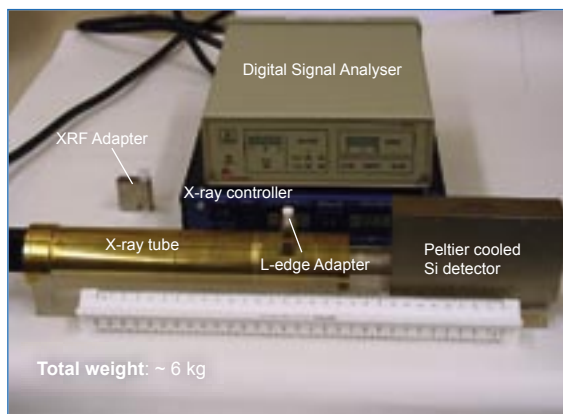


Fig. 2: Photograph of the new COMPUCEA for uranium element assay

for the analysis of solid samples. Because of this additional step of sample preparation, an assay with COMPUCEA represents more a kind of radio-analytical analysis involving careful analytical procedures (like quantitative dissolution, solution density measurements, quantitative aliquoting etc.) than a single spectrometric measurement. In the final design, a flowing-through quartz cell with a solution depth of 2 mm has been chosen for the measurement of the uranium solutions.

A prototype of the 2nd generation of COMPUCEA has been tested during some of the PIV campaigns in 2006 in parallel with the current 1st generation of equipment. An example for the comparison of the results is shown in Fig. 4. The positive practical experiences and the demonstrated measurement performance have led to the decision to employ the new COMPUCEA from 2007 onwards as routine Safeguards measurement tool.

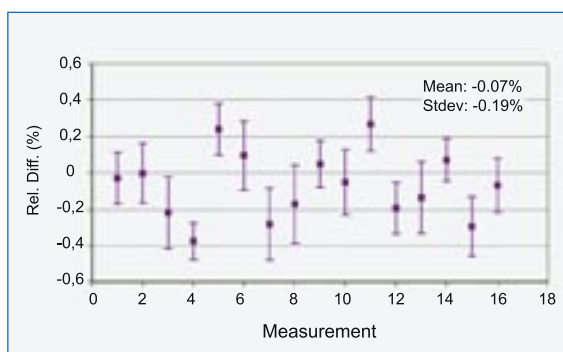


Fig. 4: Relative difference between uranium concentrations measured with COMPUCEA 2nd and 1st generation

1. Safeguards Research and Development

Operation of the On-Site Laboratories

Both on-site laboratories, the OSL (On-Site Laboratory) at the British Nuclear Group (BNG) reprocessing plant in Sellafield, (UK) and the LSS (Laboratoire sur site) at the Areva NC reprocessing facility in La Hague (France) have been operated by staff of ITU for more than six years on behalf of DG TREN. In line with the European Commission's obligation arising from the Euratom treaty to „satisfy itself that nuclear material are not diverted from their intended uses as declared by the users”, discussions took place during the construction of both reprocessing plants in the mid 1980s on the implementation of safeguards measures. Taking into account all aspects it was concluded that the most timely and cost-effective manner for verification analysis of samples taken by DG TREN inspectors could be achieved by on-site laboratories: i.e. bringing the analysts to the nuclear material rather than transporting the samples to specialised „off-site“ analytical laboratories [2,3]. Although very different in infrastructure and type of samples to be analysed, both on-site laboratories are based on the same analytical approach: radiometric methods are used as so-called „workhorses“ analysing the majority of incoming samples while isotope dilution mass spectrometry (IDMS) and thermal ionisation mass spectrometry (TIMS) are applied to at least 10 % of the samples for internal quality control. External quality control is achieved through participation in inter-laboratory programs, as organised by Cetama (EQRAIN) and IRMM (REIMEP). The results obtained have demonstrated the continuous high accuracy of the results (uranium and plutonium element assay and isotopic composition). Fig. 5 and Fig. 6 show the total number of samples analysed over the six years of operation and the distribution of sample types.

The new safeguards approach introduced by DG TREN in 2005 had only a limited influence on the sample taking at the Sellafield plant. The major reason for the decrease in the number of analysed samples is related to the temporary closure of THORP (Thermal Oxide Reprocessing Plant) due to a pipe work failure in April 2005. There was, however, an increase in so-called „special“ samples that require more intensive analyses as they fall outside the criteria for routine measurements.

Thanks to increased efficiency in the laboratory, streamlined procedures and build up of site specific

experience the average weekly presence of ITU analysts in the OSL decreased from 3.4 in 2000 to 2.7 in 2006. The OSL staff has since 2004 been involved in scrutinising the analytical results of the plant operator. In 2006 the OSL has taken over the responsibility to operate also the hybrid K-edge instrument installed in THORP for the measurement of dissolver solutions for U and Pu element assay and density determination.

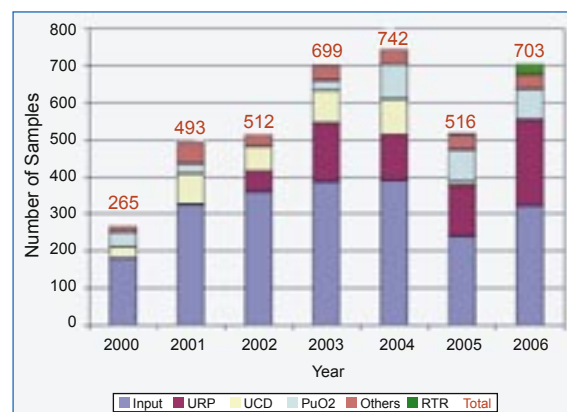


Fig. 5: Number of samples analysed in the LSS (La Hague) and distribution according to sample type

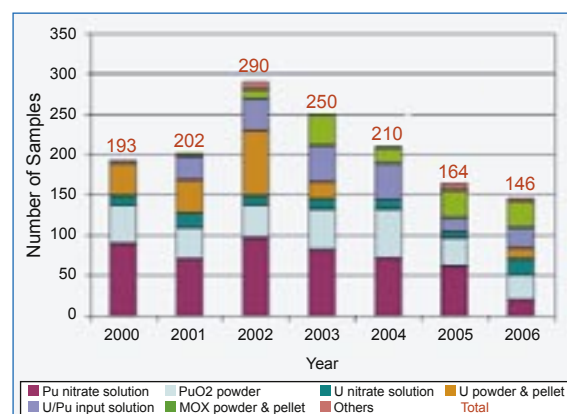


Fig. 6: Number of samples analysed in the OSL (Sellafield) and distribution according to sample type

The instrument has been repaired, calibrated, and prepared for high quality measurements in view of the re-start of THORP foreseen in 2007.

Also in the LSS an increase in efficiency could be reached through the experience gained and by optimisation of processes. This is reflected in the average number of ITU analysts present on site each week, which could be reduced from 4 to 3 between 2000 and 2006. In 2005 and 2006 several batches of spent

fuel arising from research and test reactors (RTR) have been reprocessed resulting in higher enriched uranium samples requiring additional mass spectrometric measurements. Nine samples arising from the reprocessing of spent MOX fuel have required measurements by isotope dilution mass spectrometry (IDMS) to assure the accuracy of the results. Furthermore, PuO_2 powders produced from this „second generation“ Pu are in the process of being measured.

Over the six years of operation both on-site laboratories have demonstrated their ability to adapt to changes in plant operation, in sample composition and in the safeguards approach. Technical problems arising during the operation were solved and measurement results of the highest accuracy were delivered to DG TREN, enabling them to draw proper safeguards conclusions. However, the aging of the equipment (measurement instruments and informatics) necessitated replacement and upgrading in order to maintain the high quality of the service provided so far.

The new safeguards approach of DG TREN has introduced in 2005 shifts of the responsibility for the detection of significant and small quantities of missing nuclear material towards the operator. The near real time accountancy system of the operators must be sensitive enough for detecting losses or removals of nuclear material. The results of the physical inventory verification (PIV) and the physical inventory taking (PIT) provide proof of the effectiveness of the operator's system. The on-site laboratories are essential for delivering timely and accurate analyses results of PIV samples, which form the cornerstone of the new safeguards approach. The analyses performed on the parallel samples taken at different sampling points remain important as they provide an independent confirmation of the declarations and indicate biases in the operator's analysis methods.

Environmental particle analysis for safeguards purposes

In order to achieve the non-proliferation objective of preventing further spread of nuclear weapon technology and nuclear materials that can be used for the production of nuclear weapons, the Safeguards Authorities need to apply the most advanced techniques available. A main tool for detecting undeclared nuclear activities is particle analysis performed on dust samples which were collected by safeguards

inspectors. They use cotton swipes for sample taking. The measurement techniques currently applied for analysing individual, sub-micrometer-sized particles have proven to be extremely sensitive and effective for the determination of the isotopic enrichment of uranium particles.

The ITU has been active in this field for several years, and its capabilities have been recognized with its early membership to the IAEA's Network of Analytical Laboratories (NWAL). The annual number of samples analysed at ITU for IAEA, DG-TREN and a few external customers has stabilised at about 100 – 120 per year (see Fig. 7).

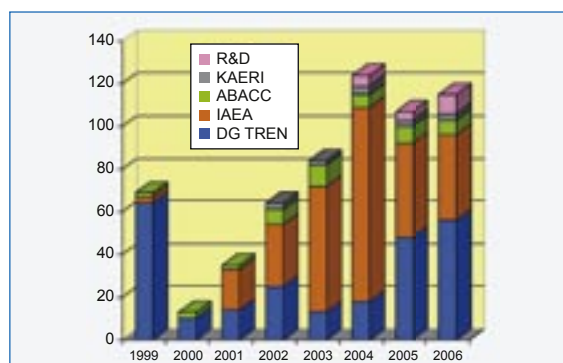


Fig. 7: The number of environmental samples analysed by SIMS at ITU. (1999 includes early test and baseline samples). After this, a continuous increase can be seen until the maximum capacity of 100-120 samples per year was reached.

ITU is using for these measurements a technique based on Secondary Ion Mass Spectrometry (SIMS). The IAEA has repeatedly asked the NWAL to strengthen its efforts in enhancing its technical capabilities and increasing its capacity. In particular the improvement of the measurement precision of the minor isotopes (^{234}U and ^{236}U) can provide essential information about enrichment facilities and the type of feed materials they use. ITU has in the last few years made several efforts to enhance its capabilities in these analyses. This has led to significant improvements in the ability to detect and analyse sub micron particles of nuclear materials. The sample preparation technique has been streamlined by introducing the particle impactor method, which optimizes the particle transfer from the swipe to the graphite planchet (used in the mass spectrometer for measuring the particles), as shown in Fig. 8. In addition, investigations were made and test work was initiated to look at future possibilities using more sensitive equipment such as Ultra High Sensitivity SIMS (UHS-SIMS).

1. Safeguards Research and Development



Fig. 8: New sample preparation technique. A part of the collected dust particles are removed from a cotton swipe and dispersed onto a sample planchet using a vacuum impactor method.

Combating illicit trafficking and nuclear forensics

The number of seizures of nuclear and other radioactive material as reported in the IAEA database on illicit trafficking remains a reason for concern. For effectively combating this phenomenon, three elements are considered as essential: prevention, detection and response. ITU is involved in all three elements, with main emphasis on response [4].

Supporting the IAEA's office for Nuclear Security, ITU assisted in drafting three guidance documents on "Nuclear Security At Major Public Events", "National Response Plan For Unauthorized Acts Involving Nuclear And Other Radioactive Material" and "Handbook On Combating Illicit Trafficking In Nuclear And Other Radioactive Material". In June 2006 and November 2006, joint training courses were held at ITU on national response plans. Participants came from the Mediterranean countries, from the western Balkan states and from south eastern Europe.

The IAEA has also launched a Co-ordinated Research Programme (CRP) on the application of nuclear forensics in illicit trafficking. ITU's contribution to the CRP will focus on the development of appropriate analytical methods, on the interpretation of the results and on providing forensic support to IAEA member states.

Nuclear forensic support was provided to EU Member States in 2006 in three relevant cases, where nuclear material was seized. An example is shown in

Fig. 10. A sample of the solid deposit on the inner wall of a piece of metal was received at ITU for nuclear forensic investigation. The material proved to be uranium with an enrichment in ^{235}U of 89%, indicating an intended use as research reactor fuel (nominal enrichment $90\pm 1\%$) as used in Russian reactors like BOR-60, VVR, IRT, MR or IVV-2M. The chemical purity of the material was, however, fairly low. This finding suggests that the material was scrap.



Fig. 9: Workshop participants during a practical exercise measuring a radioactive sample in order to assess the radiological hazard and to identify the radioactive nuclides contained in the samples

In collaboration with the new EU Member States, three different types of pellets of nuclear fuel that had been seized in Hungary some years ago were investigated in the framework of a joint analysis. Two Hungarian experts participated in the investigations of the material. Determination of the pellet dimensions, measurement of the uranium isotopic composition and of the chemical impurities, age determination and microscopic analysis were performed. The data obtained were confronted to the nuclear materials database available at ITU. All three materials could unambiguously be attributed to their place of production and intended use.

International collaboration is essential in combating a border crossing phenomenon like illicit trafficking. In addition to the bilateral collaboration with the IAEA

and with Member States, ITU participates also in the "Border Monitoring Working Group", where the activities of the IAEA, the European Commission and the United States Department of Energy are coordinated. Furthermore, ITU is co-chairing the nuclear smuggling International Technical Working Group (ITWG), in which more than 50 experts from some 25 countries exchange technical experience. In 2006 the meeting of the ITWG was organized by ITU and held in Speyer.



Fig. 10: Piece of scrap metal with a solid deposit on the inner walls (incrustation) containing highly enriched uranium

In the framework of a TACIS project the cooperation with the Bochvar Institute continued. Two Russian experts visited ITU and provided an update of the data for UO_2 and $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel manufactured in Russia. This included relations between the initial composition of the nuclear fuel and its intended use in power reactors. Furthermore, an update was performed for MOX, UO_2 and $\text{UO}_2\text{Gd}_2\text{O}_3$ fuel (produced by Western European fuel suppliers in 2005) using data provided by the fuel manufacturers. The relational database system for support of analyses of nuclear material of unknown origin (EUR 17269 EN - ITU Annual Report 1996, p.135 and EUR 18715 EN - ITU Annual Report 1998, p.33-35, 104) was maintained.

Several new activities on combating illicit trafficking, particularly in states of the former Soviet Union, were prepared. An Administrative Arrangement between the JRC and DG-AIDCO was concluded at the end of the year, enabling work to start on the projects from 2007 onwards.

References

- [1] H. Ottmar et al., Design of COMPUCEA 2nd Generation for Simplified In-Field Uranium Inventory Verification Measurements. Proceedings of the 27th Annual ESARDA Symposium on Safeguards and Nuclear Material Management, London (GB) 10-12 May 2005
- [2] L. Duinslaeger et al., Accurate and Timely Measurements - Key to Minimizing Accountancy Issues in Bulk Handling Facilities. Proceedings of the 5th Tripartite Seminar, Obninsk (Russian Federation) 2006
- [3] P. Richir et al., The Safeguards On-Site Laboratory at La Hague June 2000 - June 2006: Six Years of Operational Experience. Proceedings of the INMM 47th Annual Meeting, Nashville (USA) 2006
- [4] K. Mayer et al., Tracing the Origin of Diverted or Stolen Nuclear Material through Nuclear Forensic Investigations; in „Verifying Treaty Compliance“ Eds. R. Avenhaus, N. Kyriakopoulos, M. Richard, G. Stein - Springer 2006

Contact:

K. Mayer, tel.: +49 7247 951 545
klaus.mayer@ec.europa.eu

karin.casteleyn@ec.europa.eu

lily.duinslaeger@ec.europa.eu

magnus.hedberg@ec.europa.eu

klaus-richard.luetzenkirchen@ec.europa.eu

herbert.ottmar@ec.europa.eu

arndt.schubert@ec.europa.eu

pieter.van-belle@ec.europa.eu

maria.wallenius@ec.europa.eu

evelyn.zuleger@ec.europa.eu

1. Safeguards Research and Development

Selected Publications

- M. Wallenius, K. Mayer, I. Ray
Nuclear forensic investigations: two case studies.
Forensic Sci. Int. 156 (2006) 55
- K. Mayer, M. Wallenius, I. Ray
Tracing the origin of diverted or stolen nuclear material through nuclear forensic investigations.
Book chapter in: "Verifying Treaty Compliance - Limiting Weapons of Mass Destructions and Monitoring Kyoto Protocol Provisions" 389-408
R. Arvenhaus, N. Kyriakopoulos, M. Richard, G. Stein (Eds.)
Springer Heidelberg (2006) ISBN 3-540-33853-5
- I. Ray, H. A. Thiele, T. Wiss
Microbeam analysis in combating smuggling of nuclear materials.
EMAS 2006 - 7th EMAS Regional Workshop on Electron Probe Microanalysis Today – Practical Aspects
Proceedings of the Conference (2006) 255-263
Karlsruhe (G) 13-16 May 2006
- M. Wallenius, S. Abousahl, K. Lützenkirchen, K. Mayer, H. Ottmar, I. Ray, A. Schubert, T. Wiss
Actinides - a challenge for nuclear forensics (invited talk).
Actinides 2005 - Recent Advances in Actinide Science - RSC Publishing (2006) ISBN 0-85404-678-X
Proceedings of the Conference (2006) 26-31
Manchester (UK) 4-8 July 2005
- M. Wallenius, K. Lützenkirchen, K. Mayer, I. Ray
Nuclear forensics investigations with a focus on plutonium.
Plutonium Futures - The Science 2006 - Lawrence Livermore National Laboratory
Proceedings of the Conference /UCRL-PROC-222342 / 63
Asilomar, Pacific Grove (USA) 10-13 July 2006
- P. Richir, K. Casteleyn, A. Guiot, M. Hild, A. Le Terrier, S. Millet, P. van Belle, K. Mayer, O. Drinnhausen, L. Duinslaeger, H. Eberle, J. Enright, J. Horta, B. Lynch, H. Ottmar, H. Schorlé, S. Street, E. Zuleger, K. Lützenkirchen
The safeguards on-site laboratory at La Hague.
June 2000 - June 2005: Experience over five years of operation.
INMM 46th Annual Meeting of the Institute for Nuclear Materials Management
Proceedings of the Conference (2006) paper 206
Phoenix (USA) 10-14 July 2005
- S. Abousahl, H. Ottmar, P. Peerani, R. Berndt
International workshop on gamma evaluation codes for plutonium and uranium isotope abundance measurements by high-resolution gamma spectrometry.
INMM 47th Annual Meeting of the Institute for Nuclear Materials Management
Proceedings of the Conference on CD-ROM (2006) paper 242
Nashville (USA) 16-20 July 2006
- S. Abousahl, H. Ottmar, H. Eberle, P. van Belle, R. Krikstolaitis
New parameter values of isotope correlations for the estimate of 242 PU.
INMM 47th Annual Meeting of the Institute for Nuclear Materials Management
Proceedings of the Conference on CD-ROM (2006) paper 241
Nashville (USA) 16-20 July 2006

Collaborations

- Austria:** A. Nilsson, S. Johnson, E. Kuhn, C. Schmitzer, D. Donohue (International Atomic Energy Agency IAEA, Vienna)
- Azerbaijan:** A. Garibov (Institute of Radiation Problems, Baku)
- Bulgaria:** J. Stamenov, V. Strezov (Institute for Nuclear Research and Nuclear Energy INRNE, Sofia)
- Czech Republic:** Z. Malek, F. Sus (Nuclear Research Centre, Rez); L. Bartak (State Office for Nuclear Safety, Prague)
- Finland:** E. Martikka, P. Karhu (Radiation and Nuclear Safety Authority STUK, Helsinki)
- France:** R. Chiappini, B. Chartier (Commissariat à l'Energie Atomique CEA, Bruyères le Châtel); M. Measer, W. E. Lippert (Interpol)
- Germany:** G. Kirchner (Univ. Bremen, Institute of Environmental Physics); M. Hoffmann, H. Walter, R. Maier (Bundesamt für Strahlenschutz, Salzgitter); K. Hampel (Max-Planck-Institut für Kernphysik, Heidelberg); J. V. Kratz, N. Trautmann (Univ. Mainz, Institut für Kernchemie); S. Limmer, D. Dittmann (Bundeskriminalamt); S. Möbius, M. Kautt, M. Hoffmann (Forschungszentrum Karlsruhe)
- Georgia:** J. Mamasakhlisi (Nuclear and Radiation Safety Service, Tbilisi)
- Hungary:** T. Biro (Institute of Isotope and Surface Science, Budapest); J. Safar (Hungarian Atomic Energy Authority, Budapest)
- Japan:** Y. Tsutaki (Nuclear Material Control Center, Tokai-mura); S. Sakurai, N. Surugaya (Japan Atomic Energy Agency, JAEA, Tokai-mura)
- Lithuania:** V. Remeikis (Institute of Physics, Vilnius)
- Luxembourg:** M. Boella, F. MacLean, P. Chare, P. Meylemans, P. Schwalbach (EC DG TREN)
- Moldova:** D. Purice (Customs Service, Chisinau)
- Netherlands:** J. Garcia (Europol, The Hague)

Poland:	G. Smagala (Central Laboratory for Radiological Protection, Warsaw)
Russia:	A. Petrov, E. Kuteynikova (All Russia Research Institute of Inorganic Materials, Moscow), I. Sazonov (All Russia Research Institute for Automatics, Moscow)
Slovakia:	J. Vaclav (Nuclear Regulatory Authority, Trnava)
Sweden:	L. van Dassen (Swedish Nuclear Power Inspectorate SKI, Stockholm)
United Kingdom:	P. Thompson, C. Hutchinson (AWE Aldermaston); S. Johnson (Springfields Fuels); N. Hodge (Nexia Solutions, Springfields)
Ukraine:	V. Tryshyn (Institute for Nuclear Research, Kiev)
USA:	S. Goldberg (New Brunswick Laboratory, Argonne, IL); S. Niemeyer, D. Phinney (Lawrence Livermore National Laboratory, CA); C. Rudy (Los Alamos National Laboratory, NM); Katherine Garner (US Department of Energy)

2. Measurement of Radioactivity in the Environment

Highlight

Mapping of Radionuclides in Biological Tissues by Secondary Ion Mass Spectrometry

In the framework of a collaboration with the Istituto di Fisiologia Clinica (CNR, Pisa) and the University of Pisa (Department of Chemistry and Industrial Chemistry), Secondary Ion Mass Spectrometry (SIMS) has been applied to study the mapping of radionuclides in biological tissues. In particular, ^{10}B has been investigated in brain tissues (Boron Neutron Capture Therapy) and ^{99}Tc in heart tissues (employed as tracer for studying some cardiovascular pathology) respectively.

In both applications, the most critical step to be evaluated was the sample preparation and preservation. Since SIMS is an instrumental technique working under high vacuum, there is a risk to destroy the biological tissue. The samples were cut with cryomicrotome, then immediately adapted on a support of indium for the analysis by SIMS and further lyophilised. Their preservation during the transport from Italy to Germany was performed in a system under low vacuum. The integrity of the tissues was verified by measuring the ratio Na/K . The results perfectly corresponded to the physiological value in a reproducible manner from sample to sample. In Fig. 1 the SIMS mapping of ^{23}Na and ^{39}K in one heart tissue sample is shown. Rationing the intensity of the two signals the Na/K ratio can be obtained on the entire sample surface analysed.

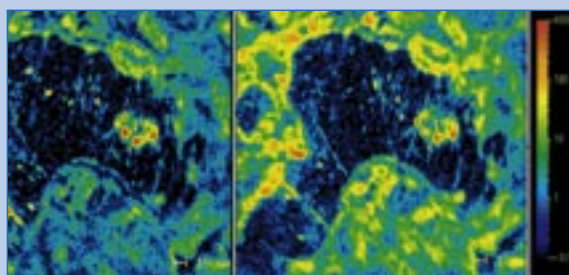


Fig. 1: Mapping by SIMS of ^{23}Na and ^{39}K in a sample of heart tissue. The scale of colour refers to the intensity of the signal

When applying BNCT, one of the main issues not yet completely solved is the optimization of the quantity of ^{10}B delivered to the tumour. The reference values for a therapeutically dosage are 10^9 atom per tumour cell. Considering the total kinetic energy of about 2.79 MeV emitted by the alpha particles produced by the splitting of ^{10}B dissipated in $10\mu\text{m}$, it would be possible to destroy the tumour without damaging the sur-

rounding tissue, providing that the absorption of ^{10}B is selective for the tumour cell. The estimation of ^{10}B , administered generally as Boro-phenilalanina (BPA), in the tissue is presently evaluated by measuring the concentration of ^{10}B in the blood. In order to quantitatively estimate the mechanism of absorption of ^{10}B , SIMS has been employed to map its distribution in the cells. A quantitative estimation has been possible by analysing the same samples analysed by SIMS, by high resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) after complete dissolution. In this way a relative sensitivity factor for ^{10}B in brain tissues has been obtained when the SIMS analysis is performed.

The mechanisms responsible for cardiac failures are different. The application of imaging techniques having high spatial resolution (much lower than mm scale) can be a solution for studying the problems related to the physiopathology of cardiovascular diseases for their prevention and treatment. The objective is to demonstrate the relationships between the microperfusion in coronary vessels and the miocardic metabolism and damage under different condition of

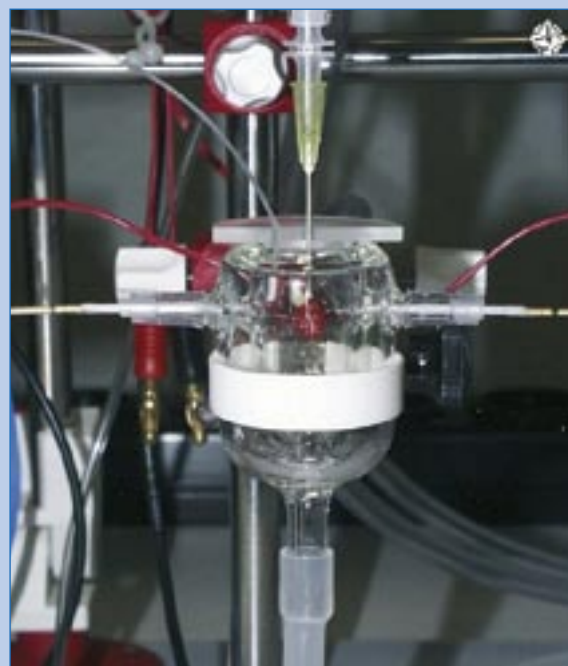


Fig. 2: Langerdoff perfusion system

heart perfusion. The possibility to use ^{99}Tc as tracer has been tested in this study. The radionuclide has been perfused in heart tissue (Langendorff model). In Fig. 2 the apparatus used for performing the Langerdorff perfusion is illustrated.

After the perfusion of the heart with a solution of N-ethyl-N-etossi-ditiocarbammato- $^{99\text{m}}\text{Tc}$ ($^{99\text{m}}\text{Tc}$ -N-NOET), the samples were prepared for the analysis by SIMS. At mass 99 an interference due to the matrix was revealed. Its extent was evaluated by performing a measurement at mass resolution of 1600 and consequently it was possible to calculate the percentage of the influence on the signal of technetium when measuring the samples for which only a mass resolution of 880 needed to be used in order not to destroy the tissue. In Fig. 3 the mass spectrum showing the separation of the interfering signal on technetium is shown.

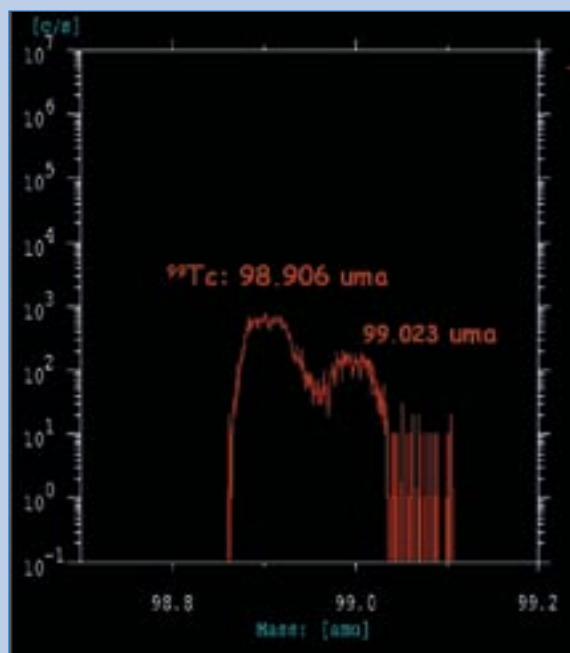


Fig. 3: Separation in the heart tissue sample at mass 99 among technetium and the interferent specie

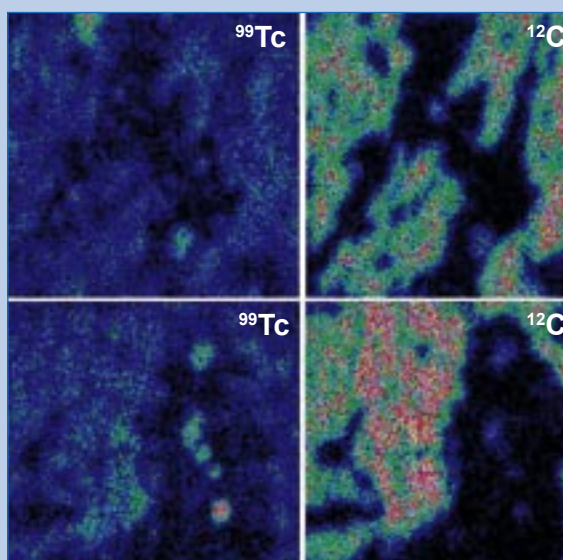


Fig. 4: SIMS mapping of ^{99}Tc in the heart tissue

The distribution of technetium was then mapped in the tissue respect to the ^{12}C that is the major matrix element. Figure 4 shows that the distribution of ^{99}Tc .

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Contact:

M. Betti, tel.: +49 7247 951 363
maria.betti@ec.europa.eu

2. Measurement of Radioactivity in the Environment

Introduction

As established in the 6th Framework Programme, scientific and technical activities in support to the policy of the Radiation Protection Unit (H4) of the Directorate General for Transport and Energy of the European Commission have been continued. These activities cover the implementation of the requirements of environmental radioactivity surveillance (Art. 31-38 of the Euratom Treaty) as well as the framework of the OSPAR (Oslo-Paris Convention) strategy on the management of radioactive substances for the protection of marine environment of the North-East Atlantic. During 2006 a method based on the use of SIMS for the mapping of radionuclides in biological tissue has been developed (see Highlight). In the framework of the Enlargement and Integration policy of the EU, the project on "Harmonisation of Techniques and Methodologies for Measuring Radioactivity in the Environment" started in 2003 has been continued with the participation of laboratories from nineteen countries. During 2006 a report summarising the results obtained during a sampling field trial performed in the Slovak Republic has been issued with the Slovakian authorities. The results will be presented at a IAEA Conference in Vienna in April 2007 and at a workshop that will take place at ITU end of June 2007.

2.1 Study on the Oxidation State of U, Pu and on the Distribution of Elements in Radioactive Environmental Particles

During 2006 two measurement campaigns were carried out at Beamline L, Hasylab Synchrotron in Hamburg. The experiments at the synchrotron facility were focused on the determination of U and Pu oxidation states as well as on the investigation of element distribution in environmental radioactive particles. Since the particles were released under different scenarios, it is expected that their physicochemical properties are related to the particular release conditions. The results of the experiments are of high importance for the radiological assessment of the contaminated areas from where the particles originate. Additionally the same techniques could be applied in nuclear forensic investigations. The overall understanding of the environmental behaviour of the radioactive particles and undergoing physicochemical processes are key factors in the assessment of the fate of U and Pu pre-

sent in the environment in the form of hot particles. The first measurement campaign (April 2006) was focused on a sediment particle found in the vicinity of one nuclear reprocessing facility. The element distribution in this particle was determined by confocal XRF-analysis. The spatial resolution of the setup was about 20 μm in all dimensions [1]. The obtained XRF spectra were analyzed with the AXIL software. Further data processing and reconstruction of elements distribution (for Ca, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Ba, Pb, U) was done with the software "R" [2] dedicated for statistical calculations. The analysis of the oxidation state of uranium present in the particle was done by the XANES technique. The absorption spectra were recorded in fluorescence mode. To determine the oxidation state of U the L_{III} absorption edge was chosen. The energy of the exciting beam was stepped in the

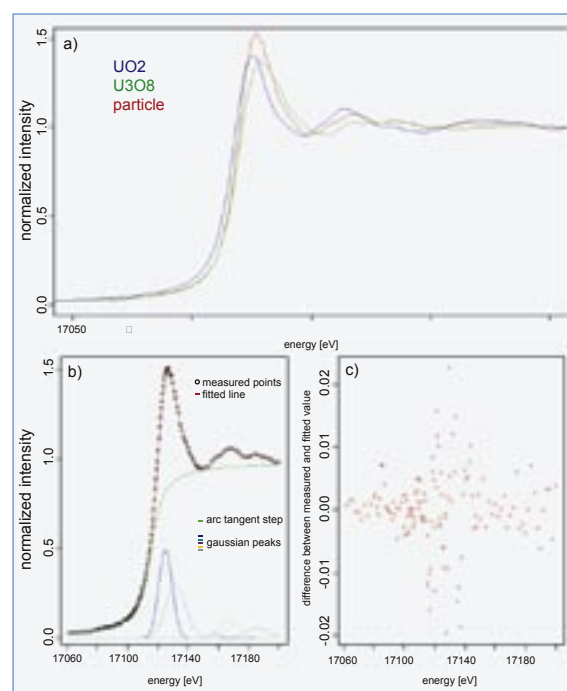


Fig. 1.a) The XANES spectra of U for the sediment particle, UO_2 and U_3O_8 samples, b) mathematical model used for fitting the experiment data, c) the residual values after the fitting expressed as difference between the measured and the fitted values.

edge region by 0.5 eV with the Si(111) monochromator. For regions further from the edge the step was increased to 1, 2 and 5 eV respectively. The region of interest was set from around 100 eV before to 200 eV after the edge. The XRF spectra were collected with fast counting energy-dispersive Silicon Drift Detector (SDD VORTEX). Then the spectra were analyzed with the AXIL as softwa-

re to obtain the $U L_{\alpha}$ intensities. The same statistical program ("R" software) was used to fit experimental data. In the mathematical model the arc tangent step and two Gaussian peaks were used to cover the edge and white line region. More peaks were used to fit the EXAFS oscillations. Confocal XRF-measurements showed that uranium is concentrated in a few discrete inclusions in the particle. For one of these inclusions XANES analysis was performed. Since the dimensions of the single inclusion were very small, the experiment was also done with confocal setup. The spectrum from the sample was compared with the spectra recorded on samples with known oxidation states (UO_2 and U_3O_8). The oxidation state determination was done as by Conradson [3]. Both the energy of the arctangent step inflection point and the energy of the white line were taken from fitting results. The XANES spectra, mathematical model used for fitting experimental data and the residual values as difference between the measured and the fitted values are presented on Fig. 1.

The XANES analysis showed that the average oxidation state of uranium (calculated with use the shift of the inflection point of the arctangent step as well as the position of the multiple scattering peak in the mathematical model fitted to the measurement data) is 5.23 ± 0.33 . This corresponds to of proportion 32 % U(IV) and 68 % U(VI), with an absolute uncertainty of 12 %. During the second campaign (October 2006) measurements were focused on XANES analysis of Pu in particles separated from soil samples of the Marshall Islands. The data obtained during this session are still under evaluation. However, the first results of XANES experiments show small shifts of the Pu L_{III} absorption edge energies registered for the different points (central and peripheral) of the same sample. This could indicate different oxidation states of Pu in the measured points, and lead to conclusion concerning the behaviour and future fate of the particle. Therefore, a more detailed investigation of the particles will be performed during the next experiments in 2007. It is foreseen to obtain from the XANES confocal experiments section maps or spatial reconstructions of particle fragments.

References

- [1] K. Janssens et al., Spectrochim. Acta B 59 (2004) 1637
- [2] R Development Core Team, R: A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, Vienna, Austria, 2006, ISBN 3-900051-07-0, <http://www.R-project.org>
- [3] S. Conradson, Los Alamos Science 26 (2006) 422

Contact:

M. Betti, tel.: +49 7247 951 363
maria.betti@ec.europa.eu

2.2 Measurements of Radioactivity in Bulk Samples

Radionuclides in foodstuff

A new revised guideline for radionuclides in foods contaminated following a nuclear or radiological emergency for use in international trade was adopted as a Codex text on July 2006. In Tab. 1 guideline levels are shown for some radionuclides in foods. The radionuclides include are those important for uptake into the food chain and are usually present in nuclear installations or used as a radiation source in large enough quantities to be significant potential contributors to levels in foods. They could be accidentally released into the environment from typically installations or might be employed for malevolent actions.

Table 1. Guideline levels (Bq/Kg) for radionuclides in foods (Codex CAC/GL 5-2006)

Radionuclides in Foods	Guideline Level (Bq/kg)	
	Infant Foods	Other Foods
^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Am	1	10
^{90}Sr , ^{106}Ru , ^{129}I , ^{131}I , ^{235}U	100	100
$^{32}\text{S}^a$, ^{60}Co , ^{89}Sr , ^{103}Ru , ^{134}Cs , ^{137}Cs , ^{144}Ce , ^{192}Ir	1000	1000
$^3\text{H}^b$, ^{14}C , ^{99}Tc	1000	10000

^a Organically bound sulfur ^b Organically bound tritium

Tab. 1: Guideline levels (Bq/kg) for radionuclides in foods

The guideline level for actinides (^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Am) in infant foods is 1 Bq/kg. In Fig. 2A the radiochemical procedure for separation Pu and Am in 25 g of baby foodstuff is shown. Plutonium and americium were determined by alpha spectroscopy after chemical separation by exchange and microprecipitation with NdF_3 on a membrane filter and after chemical separation using a combination of TEVA and anion exchange resins, respectively. In Figure 1B and 1C typical spectra relevant to separated plutonium and americium are given corresponding to an activity of 15 and 17 mBq of plutonium and americium, respectively.

2. Measurement of Radioactivity in the Environment

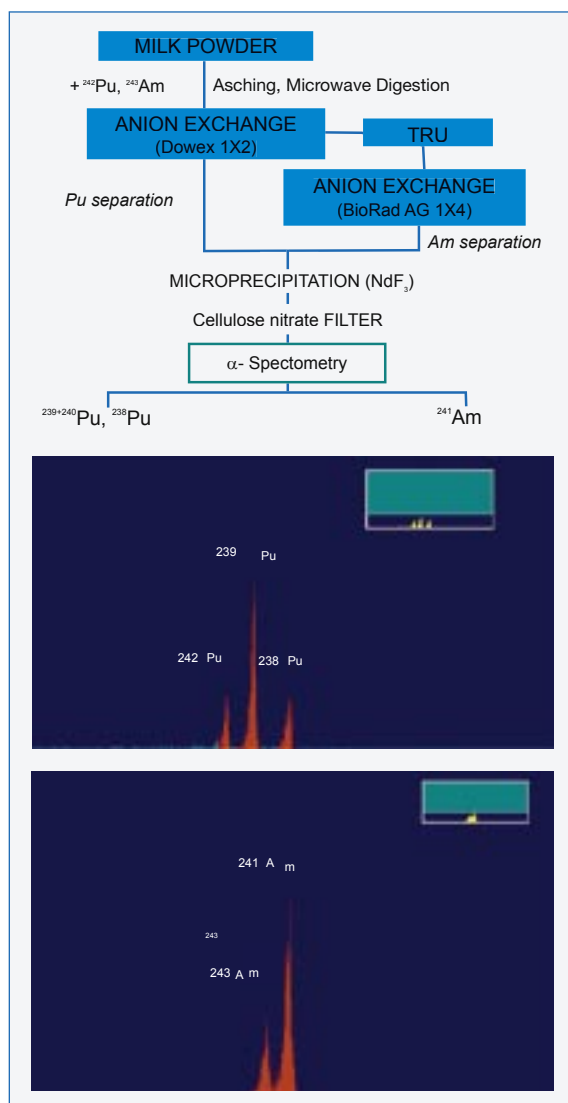


Fig. 2: Schematic procedure for the analysis of plutonium and americium by alpha-spectrometry in baby foodstuffs

Interactions uranium-proteins

Many proteins contain metal ions either within their own structures or bound to some of their active sites. In native proteins, metals can have various functions: structural role, transport through the cells, and catalysis of many reactions. The toxicological effects of many metals can be related to their ability to interact with these functions and the consequences of a metal-protein interaction could be dramatic and lead to a loss of the original biological activity of the protein. Although the various interaction processes between essential cations and proteins are widely studied, fo-

cus on the actinide family is less common. In particular, the interaction of these cations in the biologically active sites is only partially understood.

Focus on the actinide series has been motivated by risk assessments related to the wide use of nuclear fuel sources and industrial or military applications. Uranium is one of the most abundant radiotoxic elements in the geosphere on addition to Th and Pa. The natural uptake of uranium is less than 2 µg per day, mainly by the ingestion of drinking water and food. Only 0.2 % of the uranium ingested is transferred to the blood, where it is present in the oxidation state VI (UO₂²⁺), and partitioned in the serum as uranyl carbonate species (90%) and uranyl-proteins-carbonate complexes [1]. Some proteins that have been described to bind uranium with high affinity are transferrin and albumin. In addition, some proteins can also bind uranium non-specifically as peptide carboxylate ligands. In a recent in-vitro study, ten new serum proteins have been identified to bind uranium [2].

In order to understand the chemistry and the distribution of uranium in body fluids, the pathways of uranium absorption in the body and to identify new uranium target proteins, a combination of separation techniques (HPLC, capillary HPLC and capillary electrophoresis) hyphenated to high sensitive detection instruments (ICPMS, ESI-MS) has been used in our laboratory.

A protein-metal assay is shown in Fig. 3A. Apotransferrin is dissolved in HEPES-NaCl pH 7.4 buffer and supplemented with sodium carbonate and an excess of uranyl ions. After overnight incubation at room temperature and under continuous stirring, unbound uranyl ions are separated using both gel exclusion chromatography and ultracentrifugation.

In Fig. 3B the uranium distribution in the different fractions after ultracentrifugation using Microcon YM-3000 (minimal mass 3000 MW) is shown. Between 40 and 50 % of the uranium is found in the concentrate and between 20 and 25 % in the filtrate corresponding to the bound and free uranyl fractions, respectively. In Fig. 3C UV spectra from concentrate fractions are presented and showing a typical protein spectrum with a maximum at 280 nm.

Analysis of protein fractions have been then performed by HPLC using a SAX-10 anion exchange co-

lumn. In Fig. 3C typical chromatograms of glycoforms of transferrin with and without uranium are shown. The presence of uranium leads to a sensitive broadening of the most abundant isoform. In fact, no significant response, using UV detection, permits precise prediction of the distribution of uranium between transferrin fractions. The detection of uranyl-protein complexes could be resolved using an on-line ICPMS as elemental detector. Further investigations in this direction are on going. In addition, capillary HPLC coupled to ESI-MS is under development in order to separate and characterise uranyl-transferrin isoforms.

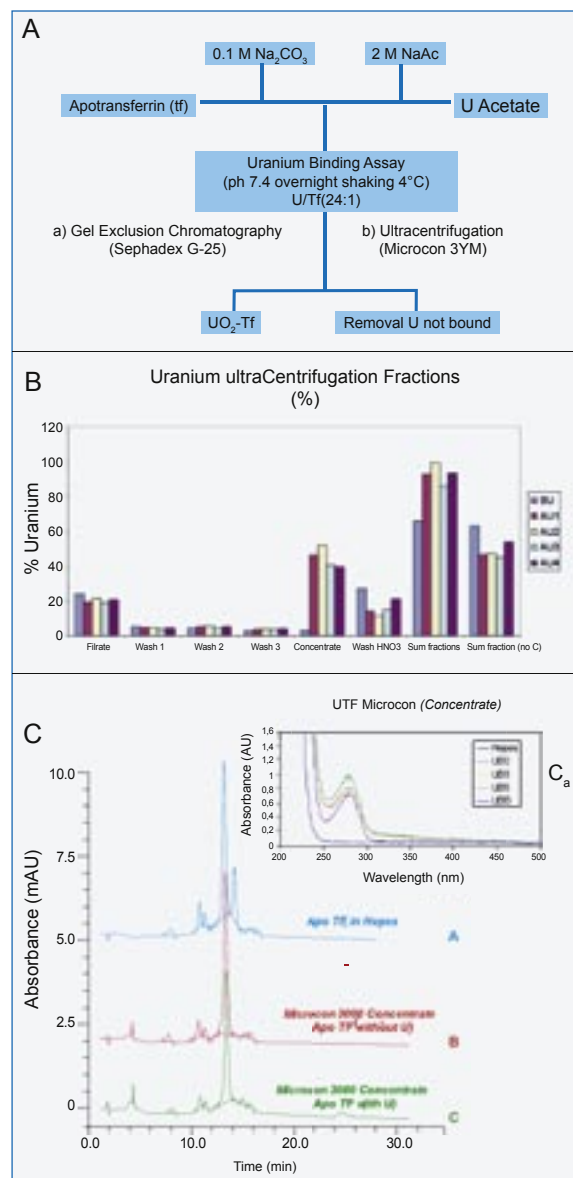


Fig. 3: Characterisation of uranium protein targets

References

- [1] J. D. Van Horn et al., *Coordin. Chem. Rev.* 250 (2006) 765
- [2] C. Vidaud et al., *Chem. Res. Toxicol.* 18 (2005) 946

Contact:

L. Aldave de las Heras, tel.: +49 7247 951 357
laura.aldave-de-las-heras@ec.europa.eu

Selected Publications

A. Pitois, A.; L. Aldave de las Heras, A. Zampolli, L. Menichetti, R. Carlos, G. Lazzerini, L. Cionini, P. Salvatori, M. Betti
Capillary electrophoresis-electrospray mass spectrometry and HR-ICP-MS for the detection and quantification of 10B-boronophenylalanine (10B-BPA) for boron neutron capture therapy. *Anal. Bionanal. Chem.* 384 (2006) 751

S. Kurunczi, J. Osán, Sz. Török, M. Betti
Environmental Studies.

In: *Handbook of Practical X-Ray Fluorescence Analysis*
Eds.: B. Beckhoff et al. ISBN 3-540-28603-9 Springer (2006) 601

M. Betti, L. Aldave de las Heras, G. Tamborini

Mass spectrometric determination of transuranium elements (review).
Appl. Spectrosc. Rev. 41 (2006) 491

J. Jernström, M. Eriksson, R. Simon, G. Tamborini, O. Bildstein, R.C. Marquez, S.R. Kehl, T.F. Hamilton, Y. Ranebo, M. Betti
Characterisation and source term assessment of radioactive particles from Marshall Islands using non-destructive analytical techniques.
Spectrochim. Acta B 61 (2006) 971

Collaborations

Australia: M. Hotchkis (Australian Nuclear Science & Technology Organisation ANSTO, Sidney)

Austria: G. Voigt (International Atomic Energy Agency IAEA, Seibersdorf, Vienna)

China: Li A. Li (Institute of Atomic Energy, Department of Radiochemistry, Beijing)

Finland: S. Salomaa, R. Pollanen (STUK-Radiation and Nuclear Safety Authority, Helsinki)

France: E. Quemener, C. Videau (Commissariat à l'Energie Atomique CEA Valrho – Service de Biochimie post-génomique & Toxicologie Nucléaire (SBTN))

Germany: H. Nies (Bundesamt für Seeschifffahrt und Hydrographie, Hamburg)

Italy: P. Salvatori (Istituto Fisiologia Clinica, Pisa); R. Fuoco (Univ. Pisa, Chem. Depart.); L. Bruzzi (Univ. Bologna, Ravenna, Env. Science Depart.)

Kazakhstan: S. Lukashenko (Institute of Nuclear Physics, Kazakhstan)

Monaco: R. F. C. Mantoura (International Atomic Energy Agency IAEA)

Russia: B. F. Myasoedov (Academy of Science, Vernadsky Institute, Moscow)

USA: T. Hamilton, A. Marchetti (Lawrence Livermore National Laboratory LLNL, CA)

3. Basic Actinide Research

Highlight

Search for Higher Oxides of Pu - A Photoemission Study

After decades of believing in a very stable PuO_2 , suitable for final storage of nuclear waste, the existence of a higher oxide, PuO_{2+x} , in presence of water was unexpectedly claimed [1]. If confirmed, this would have far reaching consequences on the strategies of storage of Pu-based waste, therefore PuO_{2+x} formation has been discussed controversially for several years now. Its existence came as a surprise, because all earlier experiments had not succeeded in producing higher Pu oxides, even under drastic oxidation conditions (ozone, NO, high pressures-temperatures) [2]. It was concluded that the PuO_2 surface was not capable of adsorbing and dissociating the oxidants. The new findings were attributed to the presence of water, which would catalyse the dissociation of oxidants (molecular oxygen) at the PuO_2 surface, prior to its diffusion into the bulk.

To test the possible formation of surface PuO_{2+x} and its stability, a series of experiments were performed, in which PuO_2 films were exposed to atomic oxygen – i.e. with no need for surface dissociation. The diagnostic tool was UPS (Ultra-Violet Photoelectron Spectroscopy) which probes the oxidation state of

1-2 atomic layers – i.e. exactly that region, where oxygen adsorbs on the solid. The oxidation state of Pu is deduced from the intensity of the Pu-5f^n line, which decreases with increasing oxidation. Extremely thin films (100 atomic layers) were used to allow fast saturation of the entire PuO_2 sample.

A schematic representation of the oxidation process is shown in Fig. 1. In a first step, the metallic Pu film is exposed to a saturation dosage of molecular oxygen (see Fig. 1, I). It readily reacts, forming first Pu sesquioxide (Pu_2O_3) with the Pu-5f^5 (Pu^{3+}) configuration (see Fig. 2a), then the dioxide with the Pu-5f^4 (Pu^{4+}) configuration (see Fig. 2b). The reduction of the Pu-5f^n emission shows the reduction of the Pu-5f^n population from $n = 5$ to $n = 4$. Even at 1000 Langmuir (L) O_2 , which is a sufficient dose to oxidise 1000 atomic layers, PuO_2 does not react further, and this is related to the lack of O_2 chemisorption. However, when exposed to atomic oxygen at room temperature (see Fig. 1 II), PuO_2 further reacts forming a higher oxide. This is well documented by the reduction of the Pu-5f^n emission at 2 eV binding energy (see Fig. 2c) and the appearance of a new oxygen line at 6 eV. Being

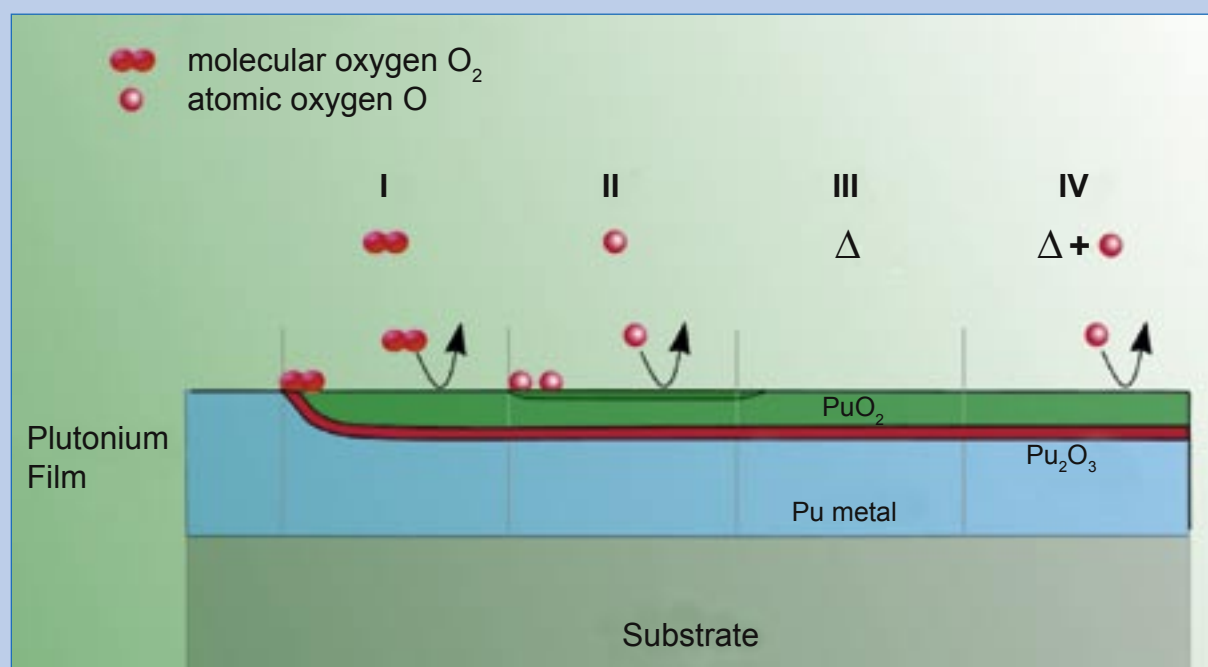


Fig. 1: Schematic description of the surface oxidation of Pu by molecular and atomic oxygen. The effect of heat is marked as (Δ).

chemisorbed at low temperature, the extra oxygen is confined to the first layer, forming surface PuO_{2+x} (see Fig. 1 II). To determine whether this surface oxygen diffuses into the film forming a stable bulk oxide, the film was heated to 200 °C (see Fig. 1 III), where diffusion could start. But under the same conditions, oxygen may also be desorbed. The basic question was, which of the two competing reactions – diffusion or desorption – takes place. The UPS spectrum (see Fig. 2d) shows, that the 5f signal grows again, i.e. the surface is reduced. However it is not possible to restore the higher oxidation state by exposing the surface to atomic oxygen at $T = 200$ °C (see Fig. 2e). The conclusion is clear: If oxygen would have diffused into the bulk, then exposing the film to a saturation dose of atomic oxygen should have allowed oxidising the entire film. This happens actually for UO_2 , which transforms completely into bulk UO_3 . PuO_2 instead does not form a higher oxide, but the surface PuO_{2+x} decomposes and oxygen is desorbed (see Fig. 1 IV).

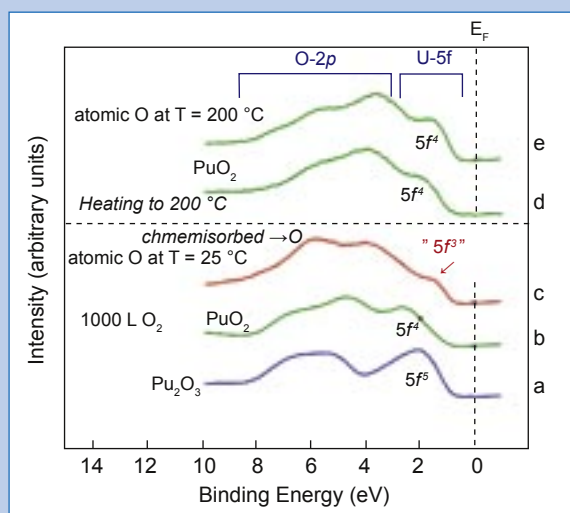


Fig. 2: UPS spectra of Pu_2O_3 exposed to molecular and atomic oxygen. Spectra marked a-e are explained in the text.

The stability of the PuO_{2+x} only as a surface phase suggests that geometrical constraints may play a decisive role in determining the oxide stability. Indeed, one explanation for the instability of PuO_{2+x} is that the extra oxygen would distort the PuO_2 lattice too much. The outer surface layer, however, could very well incorporate (chemisorb) extra oxygen. In this context it was suggested, that the higher oxide would contain additional OH^- rather than O^{2-} [3]. While O^{2-} would expand the lattice significantly due to a strong repulsion, the hydroxyl ion with its lower charge (OH^- instead of O^{2-}), causes an attenuated repulsion. The experiment does not rule out the formation of such oxy-hydroxy compounds as $\text{Pu}_4\text{O}_8\text{OH}$ [3], which would also indicate the importance of water for the formation of a higher oxidation state. Recently it was shown, that water could also play a different role from that of a redox partner. It would transform the surface of the anhydrous PuO_2 into a hydrous oxide. Further oxidation of this compound by O_2 was shown to be thermodynamically possible [4]. This work will appear in Surface Science Letters.

References

- [1] J.M. Haschke, et al., Science 287 (2000) 285
- [2] D.L. Clark, et al., The Chemistry of the Actinide and Transactinide Elements Vol. 2 (Eds. Morss, L. et al.), 813-1264, Springer (2006)
- [3] R. Penneman, et al., Actinide Research Quarterly, LALP-04-060, 9-15, Los Alamos (2004)
- [4] V. Neck, et al., (Proceedings of the Conference Plutonium Futures – The Science 2006), J. Alloys Comp., in press, doi:10.1016/j.jallcom.2007.01.159

Contact:

T. Gouder, tel.: +49 7247 951 243
thomas.gouder@ec.europa.eu

3. Basic Actinide Research

Introduction

The Basic Actinide Research action aims at positioning the JRC as the European focal laboratory for fundamental actinide materials physics and chemistry and to facilitate the understanding and control of their properties. By opening its unique experimental capabilities and infrastructure to external users, it provides world-class user facilities to strengthen the scientific and technological developments in this field. Progress is documented in open literature publications, conferences, reports, seminars, review chapters and databases.

3.1. Character of the 5f States in the Pu-Am System

Solid-state properties of plutonium are the most complex among all the elements. The proximity of the 5f states to the localisation threshold, crossed between Pu and Am, places the physics of plutonium in the area of strongly correlated electron systems, in which existing theories have only a limited predictive capability and novel cooperative phenomena emerge under not well-understood conditions. The most enigmatic of the six Pu allotropes is the large volume δ -Pu [1], which should be magnetic according to most existing theories, but in reality remains a weak paramagnet [2].

The actinides atomic volume can serve as a very sensitive indicator of the situation of the 5f states. Then, an interesting approach is to force a lattice expansion, which generally leads to a narrowing of electron energy bands, stabilising eventually magnetism in spin fluctuators [3]. An extended range of the fcc structure exists in the Pu-Am phase diagram [4] and the lattice parameter expands considerably with increasing Am concentration. Therefore, the system offers a unique possibility to study the effect of lattice expansion on Pu. On the other hand, the effect of lattice compression on Am can be only relatively small, as the compression does not reach values obtained in high pressure experiments. This work aimed to cover basic characterisation of the fcc Pu-Am system, ranging from 5 to 43 % doping of Pu with Am. An x-ray diffraction study was followed by using bulk experimental methods (magnetic susceptibility, electrical resistivity, specific heat), and the study was

complemented by photoelectron spectroscopy, consisting of core-level x-ray photoelectron spectroscopy (XPS) and high-resolution ultraviolet photoelectron spectroscopy.

Bulk properties do not show clear anomalies or abrupt variations with addition of Am that would indicate the onset of magnetic ordering or the Pu-5f localisation (as predicted by most band theories for a lattice expansion, in this case $\Delta V/V \approx 8\%$ for 40% Am). In the Pu-rich part of the Pu-Am phase diagram, the magnetic susceptibility retains its relatively low value and weak temperature dependence [5]. The electrical resistivity also maintains the characteristics observed for δ -Pu, with a broad knee and a tendency to saturation (Fig. 1). Some features in susceptibility and resistivity are reminiscent of spin fluctuators with high spin-fluctuation energy, but doping with Am does not lead to an apparent change of any spin fluctuations [5]. Similarly, the specific heat of δ -Pu samples with Am up to 20% also indicates that onset of magnetism does not appear [6]. As a main conclusion from the photoelectron spectroscopy data [5, 7], it can be said that the characteristics of the 5f states remain preserved, despite the volume expansion, in Am doped δ -Pu.

This means that δ -Pu is not close to the onset of magnetism. This is consistent with recent extended Local Density Approximation (so called LDA + U) electronic

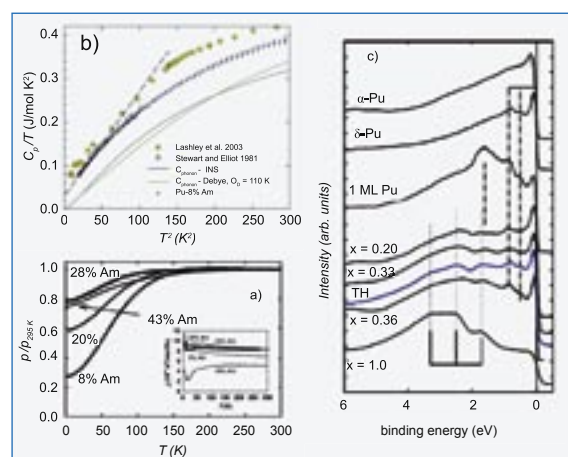


Fig. 1: a) Resistivity of selected $\text{Pu}_{1-x}\text{Am}_x$ alloys normalised to resistivity values at $T=295$ K. The insert shows UPS spectra with the Hell photoexcitation (40.81 eV). The spectra of the $\text{Pu}_{1-x}\text{Am}_x$ layers are marked by the respective x values. The vertical lines mark the position of the 5f features in pure Am and Pu-related lines. The spectrum labelled TH is "theoretical" spectrum obtained by superposition of weighted spectra of pure δ -Pu and Am.

structure calculations for δ -Pu, which yield a non-magnetic state ($S=0$, $L=0$) insensitive to volume expansion or reduced dimensionality [8, 9]. There is no visible change of the $5f$ character in doped δ -Pu (and lattice expansion) up to 20%, while the range with higher Am content remains unexplored. Therefore, δ -Pu cannot be interpreted as a simple narrow $5f$ -band system. Instead we assume that the f states are withdrawn from the Fermi level, while a many-body resonance resulting from the interaction with non- f conduction electrons can be responsible for the enhanced electronic heat capacity (Sommerfeld coefficient, γ value). The nonmagnetic character is then, as shown in [8, 9], due to the proximity to the nonmagnetic $5f^6$ state, which is reminiscent to the nonmagnetic $5f^6$ state of Am, but exhibits a rather strong hybridisation with non- f states.

References:

- [1] S. S. Hecker et al., Prog. Mater. Sci. 49 (2004) 429
- [2] J. C. Lashley et al. Phys. Rev. B 72 (2005) 054416
- [3] J. G. Sereni, J. Alloys Compd. 207/208 (1994) 229
- [4] F. H. Ellinger et al., J. Nucl. Mater. 20 (1966) 83
- [5] N. Baclet et al., Phys. Rev. B 75 (2007) 035101
- [6] P. Javorsky et al., Phys. Rev. Lett. 96 (2006) 156404
- [7] A. Shick et al., Phys. Rev. B 73 (2006) 104415
- [8] A. Shick et al., Europhys. Lett. 69 (2005) 588
- [9] A. Shick et al., Europhys. Lett. 77 (2007) 17003

Contact:

F. Wastin, tel.: +49 7247 951 387
 franck.wastin@ec.europa.eu

3.2. Thermodynamic Studies of Actinide Materials

Thermodynamic studies of molten fluoride salts containing actinides

Molten salts are of general interest to nuclear technology, as reprocessing media, as nuclear fuel, as reactor coolant, or as heat transfer medium for high temperature applications. At ITU, substantial research

is performed on the molten fluoride salts, with emphasis on the modelling and measurements of phase diagrams. In 2006 a PhD thesis was completed and defended successfully by Juliette van der Meer [1], dealing with the assessment of the $\text{LiF}-\text{BeF}_2\text{-ThF}_4\text{-UF}_4$ quaternary system as well as the modelling/prediction of the $\text{LiF}-\text{NaF}-\text{PuF}_3$ ternary system, amongst others, using a CALPHAD (Calculation of Phase Diagrams) type approach. This is a computer-based optimisation of the excess Gibbs energy of mixing (G^{xs}) of the liquid solution. Several types of mathematical and physical models were tested for the description of G^{xs} of which the sublattice model is found to be the most promising. Figure 2 shows the predicted liquidus projection of the $\text{LiF}-\text{NaF}-\text{PuF}_3$ ternary system, which is of interest for transmutation fuels of Molten Salt Reactors, as constructed from the assessed binary systems [2]. An eutectic is found at $T = 906$ K, with a composition of 53.7% LiF, 40.5% NaF, and 5.8% PuF_3 . As this temperature could be too high for fuel applications, we have studied the effect of the addition of RbF. For this purpose the $\text{LiF}-\text{NaF}-\text{RbF}-\text{LaF}_3$ proxy system was analysed [3] indicating that the $\text{LiF}-\text{NaF}-\text{RbF}$ system is a potential solvent for actinides in MSR transmutation fuels.

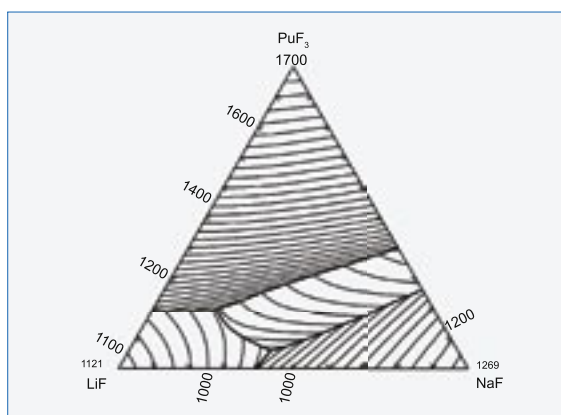


Fig. 2: Calculated projection of the liquidus of $\text{LiF}-\text{NaF}-\text{PuF}_3$. Isotherms are labelled in K, with an interval of 25 K.

Thermodynamic studies of actinide phosphates

The lanthanide orthophosphates of monazite-type structure (LnPO_4 , with Ln from La to Gd) are considered as a potential nuclear waste form. Synthetic monazite shows very promising behaviour according to various criteria for a conditioning matrix such as an incorporation of a large amount of actinide (americium and plutonium) in solid solution [4, 5]. The know-

3. Basic Actinide Research

ledge of heat capacity and entropy is indispensable for the determination of the fundamental thermodynamic functions such as the Gibbs energy e.g. to predict their stability and materials compatibility. In this context, we are investigating the thermodynamic properties of actinide orthophosphates.

PuPO_4 crystallizes in the monazite-type structure. In a previous study of the low-temperature heat capacity of PuPO_4 [6], the standard entropy of PuPO_4 was derived. Using a semi-empirical method to describe the absolute entropy, it was possible to express it as a lattice and an excess values and a good agreement was found between the experimental and estimated values for PuPO_4 , showing the validity of our estimation. From this approach, and by analogy to their

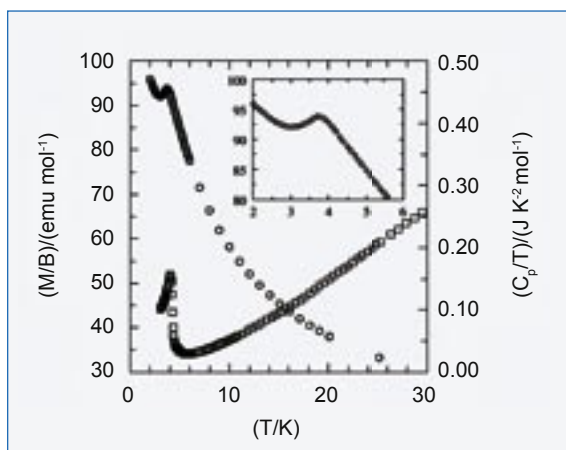


Fig. 3: Ratio of magnetisation and field (M/B) for an applied field of $B = 7$ T (O, left y-axis) and C_p/T (□, right y-axis) of $(\text{Pu}_{0.1}\text{La}_{0.9})\text{PO}_4$.

iso-electronic lanthanide compounds, the standard entropies of AmPO_4 and CmPO_4 could be estimated. However, PuPO_4 shown indications for a low-temperature anomaly, that could not be analysed in detail due to the self-heating effect. To resolve the nature of this anomaly, further measurements were made on a $(\text{Pu}_{0.1}\text{La}_{0.9})\text{PO}_4$ sample down to $T = 3$ K. Heat capacity measurements under applied magnetic field as well as magnetisation measurements revealed that the transition is probably of an antiferromagnetic ordering of the Pu^{3+} moments with $T_{\text{Neel}} = 4.1$ K (Fig. 3).

When comparing the results for $(\text{Pu}_{0.1}\text{La}_{0.9})\text{PO}_4$ with those for $(\text{Gd}_{0.1}\text{La}_{0.9})\text{PO}_4$ [7] we notice that the limiting field strength at which the antiferromagnetic ordering changes to Schottky-like behaviour is much higher for $(\text{Pu}_{0.1}\text{La}_{0.9})\text{PO}_4$ ($B_{\text{lim}} > 9$ T). The entropy of the

transition in $(\text{Pu}_{0.1}\text{La}_{0.9})\text{PO}_4$ calculated from the results is only about 0.75 of the theoretical value, whereas the value for $(\text{Gd}_{0.1}\text{La}_{0.9})\text{PO}_4$ is almost identical to the theoretical value. We attribute this discrepancy to the difficulty extrapolating the lattice heat capacity of $(\text{Pu}_{0.1}\text{La}_{0.9})\text{PO}_4$ in the relevant temperature range.

References:

- [1] J.P.M. van der Meer, PhD Thesis, Utrecht University, The Netherlands, August 2006
- [2] J.P.M. van der Meer et al., Chem. Mat. 18 (2006) 510
- [3] O. Beneš et al., Calphad 31 (2007) 209
- [4] G.J. McCarthy et al. Mater. Res. Bull. 13 (1978) 1239
- [5] L.A. Boatner et al., Inorg. Chim. Acta 94 (1984) 146 and references therein
- [6] C. Thiriet et al., J. Nucl. Mater. 344 (2005) 56
- [7] C. Thiriet et al., Solid State Comm. 134 (2005) 409

Contact:

R. Konings, tel.: +49 7247 951 391
rudy.konings@ec.europa.eu

3.3 Karlsruher Nuklidkarte: A Record of Human Achievement in Nuclear Science

For almost 50 years, the Karlsruhe Nuclide Chart has provided scientists with structured, accurate information on the decay modes of radionuclides. Beyond the more traditional physical sciences, the Chart is used widely in the life and earth sciences. The Chart is of great didactic value and is a valuable and welcome addition to many books on nuclear science.

The new 7th edition (2006) of the “Karlsruher Nuklidkarte” edited by ITU, contains new and updated radioactive decay data on 618 nuclides not found in the previous (1998) edition. In total, nuclear data on 2962 experimentally observed nuclides and 692 isomers is presented. The accompanying booklet has been considerably revised to include a history and overview of nuclear science. The multi-lingual “Explanation of the Chart of the Nuclides” has been extended to include Chinese and Russian.

Contact:

J. Magill, tel.: +49 7247 951 366
joseph.magill@ec.europa.eu

Selected Publications

- E. Colineau, F. Wastin, J. Rebizant
Magnetic anisotropy in NpRhGa⁵ single crystals.
J. Phys. Condens. Mat. 18 (2006) 411-419
- K. Kuzushita, K. Ishii, S. B. Wilkins, B. Janousova, T. Inami, K. Ohwada, M. Tsubota, Y. Murakami, K. Kaneko, N. Metoki, S. Ikeda, Y. Haga, Y. Onuki, N. Bernhoeft, G. H. Lander
Induced orbital polarization on Ga ligand atoms in UTGa₅ (T = Ni, Pd, and Pt).
Phys. Rev. B 73 (2006) 104431
- S. Raymond, P. Piekarczyk, J. P. Sanchez, J. Serrano, M. Krisch, B. Janousova, J. Rebizant, N. Metoki, K. Kaneko, P. T. Jochym, A. M. Oles, K. Parlinski
Probing the coulomb interaction of the unconventional superconductor PuCoGa⁵ by phonon spectroscopy.
Phys. Rev. Lett. 96 (2006) 237003
- S. B. Wilkins, R. Caciuffo, C. Detlefs, J. Rebizant, E. Colineau, F. Wastin, G. H. Lander
Direct observation of electric-quadrupolar order in UO₂.
Phys. Rev. B 73 (2006) 060406(R)
- P. Santini, S. Carretta, N. Magnani, G. Amoretti, R. Caciuffo
Hidden order and low-energy excitations in NpO₂.
Phys. Rev. Lett. 97 (2006) 207203
- L. V. Pourovskii, M. I. Katsnelson, A. I. Lichtenstein, L. Havela, T. Gouder, F. Wastin, A. B. Shick, V. Drchal, G. H. Lander
Nature of non-magnetic strongly-correlated state in delta-plutonium.
Europhys. Lett. 74(3) (2006) 479
- P. Javorsky, L. Havela, F. Wastin, E. Colineau, D. Bouëxière
Specific heat of δ -Pu stabilized by Am.
Phys. Rev. Lett. 96 (2006) 156404
- A. Shick, J. Kolorenc, L. Havela, V. Drchal, T. Gouder
Multiplet effects in the electronic structure of δ -Pu, Am and their compounds.
Europhys. Lett. 77 (2007) 17003
- M.E. Manley, M. Yethiraj, H. Sinn, H.M. Volz, A. Alatas, J.C. Lashley, W.L. Hults, G.H. Lander, J.L. Smith
Formation of a new dynamical mode in alpha-uranium observed by inelastic x-ray and neutron scattering.
Phys. Rev. Lett. 96 (2006) 125501
- E. Blackburn, A. Hiess, N. Bernhoeft, G. H. Lander
Inelastic neutron scattering from UPd₂Al₃ under high magnetic field.
Phys. Rev. B 74 (2006) 024406
- E. Blackburn, A. Hiess, N. Bernhoeft, M.C. Rheinstaedter, W. Haeussler, G.H. Lander
Fermi surface topology and the superconducting gap function in UPd₂Al₃: a neutron spin-echo study.
Phys. Rev. Lett. 97 (2006) 057002
- H. C. Walker, K. A. McEwen, D. F. McMorrow, S. B. Wilkins, F. Wastin, E. Colineau, D. Fort
Determination of the antiferroquadrupolar order parameters in UPd₃.
Phys. Rev. Lett. 97 (2006) 137203
- E.S. Yakub, C. Ronchi, I.L. Iosilevski
Thermodynamic model of solid non-stoichiometric uranium dioxide.
J. Phys. Condens. Mat. 18 (2006) 1227

- A. Kovacs, R.J.M. Konings
A theoretical study of the structure and bonding of UOX_x (X=F, Cl, Br, I) molecules: the importance of inverse trans influence.
ChemPhysChem 7 (2006) 455
- K. Popa, D. Sedmidubsky, O. Benes, C. Thiriet, R.J.M. Konings
The high-temperature heat capacity of LnPO₄ (Ln = La, Ce, Gd) by drop calorimetry.
J. Chem. Thermodyn. 38 (2006) 825
- K. Popa, F. Jutier, F. Wastin, R.J.M. Konings
The heat capacity of NdPO₄.
J. Chem. Thermodyn. (2006) 1306
- J.P.M. van der Meer, R.J.M. Konings, D. Sedmidubsky, A.C.G. van Genderen, H.A.J. Oonk
Calorimetric analysis of NaF and NaLaF₄.
J. Chem. Thermodyn. 38 (2006) 1260
- J.P.M. van der Meer, R.J.M. Konings, H.A.J. Oonk
Thermodynamic assessment of LiF-BeF₂-ThF₄-UF₄.
J. Nucl. Mater. 357 (2006) 48

Collaborations

- Czech Republic:** V. Sechovský, L. Havela, P. Javorský (Charles Univ. Prague); D. Sedmidubský (Institute of Chemical Technology, Prague); A. Shick, V. Drchal (Institute of Physics, ASCR, Prague)
- France:** N. Bernhoeft, J.-P. Sanchez, S. Raymond (CEA, Grenoble); A. Hiess (ILL, Grenoble); V. Klosek, P. Faure, T. Lebihan, N. Baclet (CEA-Valduc, Is sur Tille); E. Simoni, C. Lenaour (IPN/Univ. Paris XI, Orsay); W. G. Stirling, C. Detlefs, S. Wilkins (ESRF, Grenoble); A. Scheinost (ESRF-ROBL, Grenoble); K. Behnia (EPSCI, Paris); C. van der Beek (CNRS-Palaisseau)
- Germany:** K. Prokes (Hahn-Meitner-Institute, Berlin); W. Häußler (Technische Universität München)
- Hungary:** A. Kovács (Budapest Univ. Technology and Economics)
- Italy:** G. Amoretti, P. Santini, N. Magnani (Univ. Parma)
- Japan:** N. Metoki, K. Kaneko, A. Nakamura, T. Hotta, Y. Haga (ACSR, JAEA, Tokai); Y. Onuki (Osaka Univ.); Y. Shiokawa, D. Aoki, Y. Homma (IMR, Tohoku Univ, Oarai); K. Ishii (SPRING 8, JAEA, Hyogo)
- Netherlands:** H. Oonk, J.C. Miltenburg, A.C.G. van Genderen (Utrecht Univ.)
- Poland:** D. Kaczorowski, R. Troc (Int. Low Temp. & Struct. Res., PAS, Wroclaw), P. Piekarczyk, K. Palinski (Polish Acad Sci, Inst Nucl Phys, Krakow); A.M. Oles (Jagellonian Univ., Krakow)
- Russia:** I. Iosilevski (Moscow Institute of Physics and Technology, State University, Moscow)
- Sweden:** B. Johansson, P.M. Oppeneer (Uppsala Univ., Uppsala); P. A. Korzhavii (Royal Institute of Technology (KTH), Stockholm)
- UK:** K. McEwen, H. Walker (Univ. College London)
- USA:** E. Bauer, J. Sarrao, J. D. Thompson, J. Lashley, J. A. Lawson, M.E. Manley (Los Alamos Natl. Laboratory, NM); R. G. Haire, M. Yethiraj, (Oak Ridge Natl. Laboratory, TN); H. Sinn, A. Alatas (Argonne National Laboratory, IL)

4. Spent Fuel Characterisation

Highlight

Effects of Alpha-decay Damage and Helium Accumulation in High Level Waste Forms

The civilian nuclear power industry generates yearly about 10,000 tons of spent nuclear fuel including long-lived fission products and actinides produced during the irradiation of UO_2 or MOX fuels. Two main concepts are adopted today for the conditioning and safe disposal of this high-level radioactive waste (HLW): a) direct disposal of spent fuel elements; b) reprocessing of spent fuel with recycling of U-Pu, and immobilization in borosilicate glass of the remaining HLW. In both cases, the conditioning is followed by disposal in deep geologic repositories. Disposal matrices (waste forms) alternative to glass are also considered, with the basic idea of incorporating HLW produced by existing and future fuel cycles, and also excess weapons plutonium (in the United States) in the crystalline lattice of synthetic minerals, whose natural analogues are known to be very durable (they survived on our planet for billions of years). These minerals include silicates, phosphates (monazite, apatite), and titanates (pyrochlores, zirconolites).

The mechanical stability of all these materials over long aging times, coupled with a strong chemical durability, are necessary requirements to ensure that the waste forms will fulfill their expected function, which is to act as the first barrier against the release of radiotoxic species in the environment. The evolution of thermo-mechanical properties, in turn, will be determined by the effects due to accumulation of alpha-decay damage and helium in the waste materials.

The evolution of mechanical properties as a function of time/damage for materials under accelerated alpha-decay rate conditions can provide valuable information to predict the long term integrity of spent fuel and other ceramic waste forms of interest for performance assessment of a geologic repository. A multi-faceted research program is ongoing at ITU to investigate the long term stability / integrity of different types of HLW by assessing the helium behaviour and the ultimate effects of damage ingrowth (EUR 22105 EN - ITU Annual Report 2005, p. 45, [1-4]). Loading waste matrices (including UO_2) with short-lived alpha-emitters, e.g. ^{238}Pu , is a technique often used to accumulate decay dose levels corresponding to very long storage times within experimentally acceptable timeframes.

This type of information is compared with similar data obtained from alpha-doped UO_2 with very high integrated dose, and also with irradiated fuel, in order to extend the range of accumulated dose investigated and to try and understand the process and the effects of radiation damage and waste due to fission and decay.

A question often raised is the representativeness of data obtained with accelerated decay accumulation techniques such as alpha-doping. Possible decay rate effects would limit the usefulness of such methods. Work performed over more than 8 years using alpha-doped UO_2 containing ^{238}Pu has provided evidence that property changes measured for high alpha-activity materials over short-term intervals can be representative of lower activity compounds over much longer time periods.

Figure 1 shows the evolution of the Vickers hardness as function of accumulated damage for $(\text{U}_{0.999}, ^{238}\text{Pu}_{0.001})\text{O}_2$ and $(\text{U}_{0.9}, ^{238}\text{Pu}_{0.1})\text{O}_2$. The two materials accumulate decay damage at a rate differing by two orders of magnitude. The highest level of damage shown in Fig. 1 corresponds to storage periods of thousand or tens of thousand years for typical LWR fuel. In spite of the different decay rates, the evolution of the measured property (in this case hard-

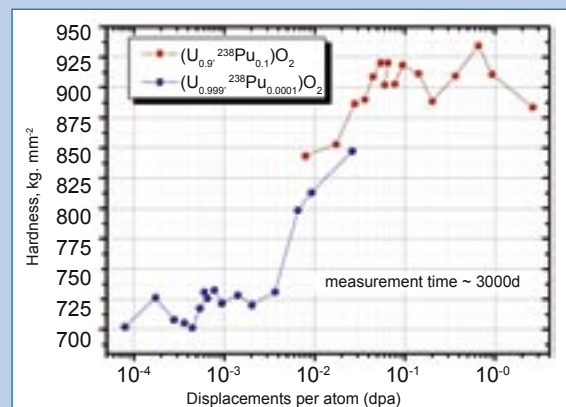


Fig. 1: Evolution of the Vickers hardness of two ^{238}Pu -doped UO_2 specimens as function of cumulated damage dose. The total time span of the measurements covered ~8 years. The increase in hardness in this case would result in a more fragile behaviour of the material which may lead eventually to pulverization of the ceramic form.

ness) is the same, showing an essentially continuous evolution independent from the time necessary to reach a given dpa (displacements per atom) level. This important finding is confirmed by other types of analysis: for instance, microstructure analysis by transmission electron microscopy revealed that the damage accumulation pattern up to a few dpa is characterized by the production of dislocation loops whose size and density increase with alpha-dose, independently from the rate (EUR 22105 EN - ITU Annual Report 2005 p. 46).

Figure 2 shows the microstructure corresponding to an extreme case of alpha-damage accumulation, a $^{238}\text{PuO}_2$ sample ~ 30 years since fabrication. The material had collected an integrated dose of about 100 dpa, one order of magnitude more than the integral decay dose accumulated by LWR spent fuel over 10^6 years, but one order of magnitude less than the fission damage dose in LWR fuel at discharge from a reactor. After 30 years the Pu oxide material had lost its integrity and was pulverized, while retaining a fraction of about 30 % of the radiogenic helium. Helium content and release behaviour were measured by thermal desorption coupled with mass spectrometry. The release started at about 800 K which is above the expected normal temperature of a geologic repository. TEM examination revealed the

presence of a high concentration of homogeneously distributed helium bubbles with size of about 5 to 7 nm. Instead of the large concentration of dislocation loops, typical of the damage levels up to a few dpa, extended dislocation networks were observed.

References

- [1] V.V. Rondinella et al., Proc. ICEM '05, Glasgow (UK), ASME 2005, CD-ROM paper 12755-8
- [2] T.A.G. Wiss et al., J. Nucl. Mater. 352 (2006) 202
- [3] V.V. Rondinella et al., Radiochim. Acta 88 (2000) 527-531
- [4] T.A.G. Wiss et al., J. Nucl. Mater., 362 (2007) 431-437

Contacts:

T. Wiss, tel.: +49 7247 951 447
thierry.wiss@ec.europa.eu

J.-P. Hiernaut, tel.: +49 7247 951 385
jean-pol.hiernaut@ec.europa.eu

V.V. Rondinella, tel.: +49 7247 951 279
vincenzo.rondinella@ec.europa.eu

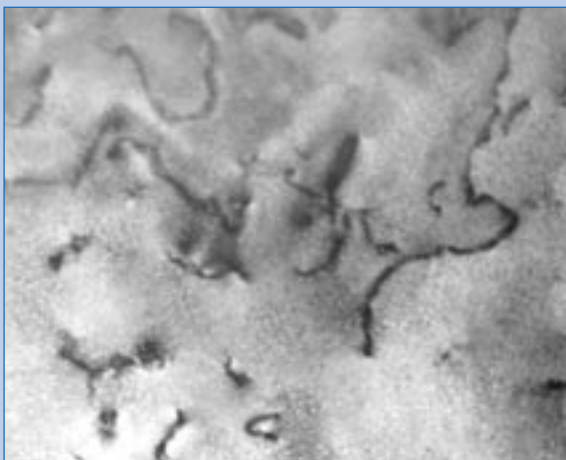


Fig. 2: Transmission Electron Microscope micrograph showing the high density of He-bubbles and the dislocation network present in a $^{238}\text{PuO}_2$ sample after accumulating 100 dpa of alpha decay damage ($\sim 5 \cdot 10^{20}$ alpha-g $^{-1}$).

4. Spent Fuel Characterisation

Introduction

The activities on Spent Fuel Characterisation continued along the pre-defined lines of study (EUR 22105 EN - ITU Annual Report 2005 p. 42). Important progress took place concerning the effects of alpha-decay damage accumulation in solid waste form. Unequivocal evidence was obtained that the microscopic alterations and the macroscopic property changes associated with accumulating radiation damage are determined by the integral decay dose accumulated and are not dependent on the dose rate, at least within the range of activities considered in our experiments. These findings validate the approach used in recent years to study the effects of decay damage, based on the characterization of materials containing short-lived alpha emitters.

Furthermore, significant progress was made in understanding the effects of radiation damage over a very broad range of integrated dose in spent fuel. Similar work is ongoing for other waste forms. The ultimate goal will be to provide a comprehensive treatment of radiation damage effects covering decay damage accumulation during storage/disposal and linking it with fission and decay damage occurring in-pile. The studies on the corrosion enhancing effect of alpha radiolysis and corrosion suppressing effect of hydrogen were focused on the mechanisms responsible for the behaviour observed previously. The role of iron was also considered.

Tests to determine the instant fission gas release fraction for high burnup UO_2 as a function of radial location, burnup and groundwater composition continued in a hot cell. A new approach was introduced to perform source term studies on MOX fuel: the Knudsen cell method was used to estimate the grain boundary inventory of the fuel, in addition to traditional leaching tests. Similar parallel analyses were performed to compare the information obtained from leaching with the outcome of electrochemistry measurements. A new leaching autoclave was introduced in a hot cell to perform corrosion studies on high burnup fuel under repository condition. The investigations on Pu-containing fuels and waste forms were extended to the case of $(\text{Th}, \text{Pu})\text{O}_2$ compounds. Moreover, new data were obtained, showing incorporation of actinides in secondary phases formed on corroded iron under reducing conditions.

Finally, modeling activities aiming at predicting properties and mechanisms or explaining measurements relevant to the evolution of radiation damage effects in oxide and advanced fuel are underway. Links and collaborations with external partners were maintained and extended, including a promising new collaboration with a sister Action in IE-Petten on the evolution of spent fuel cladding properties during storage.

Contact:

V. V. Rondinella, tel.: +49 7247 951 279
vincenzo.rondinella@ec.europa.eu

4.1 Electrochemistry, Hydrogen Effect and Radiolysis

Comparison of leaching rates with electrochemical corrosion rates

Corrosion can be defined as a weakening of the material combined with a change of thermodynamic properties. This means that corrosion does not only include mass loss by leaching, but also other reactions like surface and/or matrix oxidation, passivation, surface film formation due to precipitation. Electrochemical corrosion tests consist of differential measurements at the solid/liquid interface. The result of such a measurement is, or is directly proportional to a rate. In contrast, leaching experiments provide integral measurements (except dynamic leach tests) in the liquid phase. They give concentrations, masses or moles in solution at a given time, from which rates have to be derived by normalization and differentiation (see Fig. 1).

A comparison was carried out on results obtained from electrochemical corrosion testing and simultaneous solution analysis during long-term experiments on alpha-doped UO_2 under N_2 and N_2/H_2 purging (EUR 22105 EN - ITU Annual Report 2005 p. 43).

At the beginning of the experiment, under N_2 purging, the U-concentration in solution increased, and the derived rates matched the electrochemically measured rates well. After switching to N_2/H_2 purging, the U-concentration started to decrease, as previously seen in leaching experiments. However,

the calculation of the integral leaching rates led to values over one order of magnitude higher than the electrochemically measured corrosion rate. In this case, the electrochemical measurement follows the dissolution reaction at the solid/liquid interface, and provides an immediate measure of the actual corrosion reactions, while the response time of the concentration level in solution to a change in the corrosion rate is much slower, due to the inertia associated with the amount of material dissolved during the previous stages of the experiment.

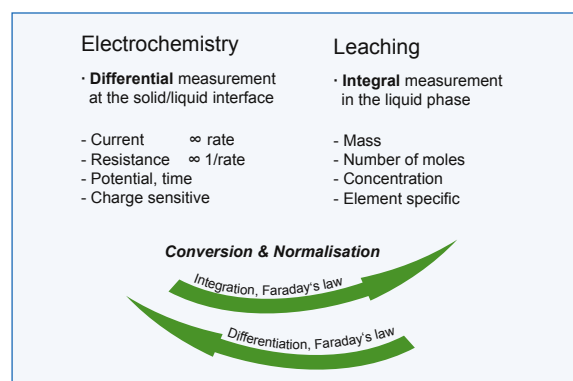


Fig. 1: Schematic relationship between electrochemistry (differential) and leaching (integral) measurements

Contact:

D. Wegen, tel.: +49 7247 951 364
detlef.wegen@ec.europa.eu

Studies on hydrogen corrosion suppressing effect

The behaviour of high burn-up fuels under repository conditions is becoming more important as reactor operators utilize the fuel more efficiently. In particular, investigating the corrosion of the rim structure is required since this is the part of the fuel that will first come in contact with water in a nuclear waste repository. New procedures have been developed to prepare suitable fragments of fuel from the rim region of a pellet in a fuel rod. An autoclave setup has been designed to corrode high burn-up fuel in a closed system under different H_2 pressures (EUR 22105 EN - ITU Annual Report 2005 p. 40) and thereby allowing a mass balance study of the system. The stable radiolytic products H_2 and O_2 will be analyzed in situ and by gas mass spectrometry, while H_2O_2

will be analyzed by spectrophotometry (see below). Additionally, pH and E_h potential will be recorded. The experiment is expected to run for several years. The corroded fuel will be characterized at the end of the experiment. Since the autoclave will operate under 50 bar H_2 for years, it is important that the leak rate is very low (<0.01 bar/h). This in turn requires highly accurate leak rate measurements to be available. An overall leak rate of 0.0012 bar/h was measured over a period of seven days on the final autoclave setup. The final autoclave setup was introduced into a hot cell and loaded with high burn-up (rim) fragments of fuel. The autoclave will be in full operation in Spring 2007.

Contact:

P. Carbol, tel.: +49 7247 951 178
paul.carbol@ec.europa.eu

Radiolysis studies

Reaction of H_2O_2 with solid actinide oxides

Information on the concentration level and the stability of H_2O_2 , the main oxidant produced during alpha-radiolysis, is important in order to determine the reaction path of spent fuel in the repository.

The rate of H_2O_2 decomposition in the presence of solid UO_2 , NpO_2 and PuO_2 was investigated, partly in collaboration with KTH (Sweden – Actinet partner). H_2O_2 solution ($\sim 10^{-2}$ M) was exposed to $^{238}UO_2$, $^{237}NpO_2$, $^{238}PuO_2$ and $^{239}PuO_2$ powders and the concentration of H_2O_2 was measured as a function of time. The decomposition rate of H_2O_2 was dependent on the actinide used (see Fig. 2). With uranium, the H_2O_2 concentration dropped below the micromolar level within a few hours; with neptunium, decomposition took ~ 8 days; with ^{239}Pu the decomposition was slower, requiring ~ 5 weeks to drop below 10^{-6} M. In the case of the short-lived alpha-emitter ^{238}Pu , a much slower decomposition rate was observed. This behaviour is likely due to surface area effects, and will be further investigated by analyzing the results of the actinides concentration measurements that are currently underway. The concentrations of H_2O_2 produced by radiolysis induced by Pu decay (also shown in Fig. 2) were orders of magnitude lower than the initial added H_2O_2 level and should not have

4. Spent Fuel Characterisation

affected the decomposition pattern of the peroxide, at least in its first stages.

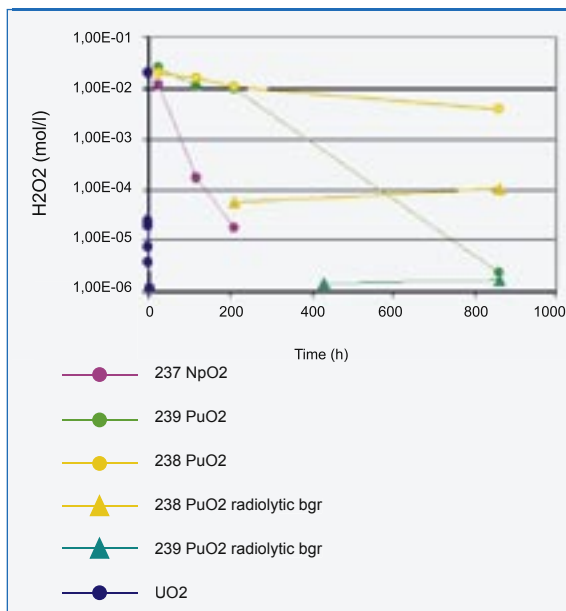


Fig. 2: H_2O_2 decomposition in presence of uranium neptunium and plutonium oxides. Hydrogen peroxide concentration vs. time. The triangles represent radiogenic H_2O_2 produced by radiolysis.

Contact:

R. Pehrman, tel.: +49 7247 951 416
reijo.pehrman@ec.europa.eu

Low concentration hydrogen peroxide determination

The measurement of very low H_2O_2 concentration (and, possibly, of radical species) would constitute a very important tool for the investigation of corrosion reactions that may be relevant for the case of spent fuel in a repository environment.

Typical concentrations of H_2O_2 formed by alpha-radiolysis are 10^{-6} - 10^{-9} M, too low for most methods commercially available. The technique used should also be adapted for operation in a small space inside a glovebox or a hot cell. Possible radical detection methods are limited and generally not available for radioactive samples. Two techniques for measurement of low concentrations of hydrogen peroxide are currently under development at ITU.

a) Spectrophotometric measurement of the tri-iodide cation, I_3^- , produced by the reaction of hydrogen peroxide with a potassium iodide solution in acidic environment. The equipment, to be installed in a hot cell, consists of a UV light source (I_3^- shows a maximum absorption at 350 nm), a holder for quartz cuvettes with 1cm path length and a spectrophotometer. The light source, the cuvette holder and the spectrometer are interconnected by optical fibre. The optimum conditions for running the measurements were obtained at pH 3 using ammonium molybdate as catalyst. The prepared solutions could be analysed immediately after adding the reagents. In these conditions the lowest detectable concentration is now $3 \cdot 10^{-7}$ M H_2O_2 . In future, the detectable concentration may be lowered to 10^{-9} M H_2O_2 using a measuring cell with a longer path length (1 m).

b) Chemiluminescence (CL) is considered a selective and sensitive method for analysis of H_2O_2 and also of OH radicals. Four hydrogen peroxide and two hydroxyl radical detection methods were modified to work with the Junior LB 9509 luminometer and tested for performance in view of future installation of the set-up in a glove box. The luminol-microperoxidase method proved to be the most suitable for the analysis of H_2O_2 and the phthalic hydrazide method for qualitative detection of hydroxyl radicals in our typical leaching experiments. Luminescence was linear for 10^{-6} - 10^{-9} M H_2O_2 solutions with a detection limit of $5 \cdot 10^{-9}$ M. Microperoxidase decomposes at room temperature, so the validity of the calibration needs to be checked regularly. The radical determination is still semi-quantitative, and more prone to uncertainties and difficulties caused by the specific conditions of the measurements.

Contact:

a) C. Alecu, tel.: +49 7247 951 490
catalin.alecu@ec.europa.eu

b) R. Pehrman, tel.: +49 7247 951 416
reijo.pehrman@ec.europa.eu

4.2 Studies on the Corrosion Behaviour of Pu-containing Fuel

Corrosion of (Th,Pu)O₂ in groundwater

PuO₂, ThO₂, and solid solution (Pu-Th)O₂ (the so-called „Th-MOX“) with 9 and 30% Pu are studied. The aim of this work is to characterize the leaching behaviour of Th-based compounds in order to assess their performance as waste form for final disposal options. Batch leaching tests are carried out at room temperature at different pH in deionized and carbonated water under deaerated conditions. To investigate the behaviour of Pu and the corrosion products, and to characterize possible secondary phases controlling the solubility of these materials, a sequence of leaching experiments is coupled with pre and post-leaching characterisation of solid phase and solutions. Preliminary solution analysis results from the first batches of tests (the experiments are still running) are shown in Fig. 3. The diagram shows the concentration of Pu in solution after approximately 130 days of leaching. The data points at the lowest

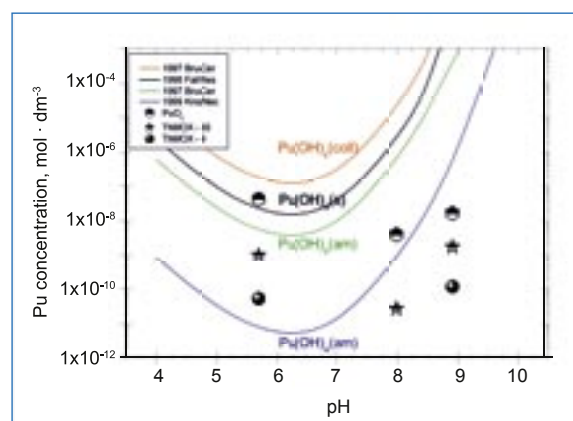


Fig. 3: Leaching of (Th_{1-y},Pu_y)O₂ with $y = 1.00, 0.30, 0.09$, respectively. Plutonium concentration in solution after ~4.5 months of leaching at different pH levels. Calculated solubility curves for different Pu species are also shown for comparison.

pH are from tests performed in deionized water, while the results at pH 8 and ~9 refer to leaching in carbonated water. At a given pH, the measured Pu concentration is increasing with increasing Pu content. The results in the diagram are compared to calculated solubility curves in equilibrium with Pu colloids [1], Pu crystalline [2] and Pu amorphous phase [3].

The concentration of Pu in solution reached during the test on PuO₂ in deionized water at pH 5.7 corresponds to the solubility controlled by crystalline Pu hydroxide [2], while the results at higher pH in carbonated water are closer to the solubility curve for amorphous phase [3]. The data for the solid solution samples are not matching solubility curves for pure Pu and Th oxides. In fact, during the elapsed contact period the dissolved concentration of Th remained very low ($10^{-11} - 10^{-10}$ M) and did not show any significant trend. The analysis of the leached surfaces may help to achieve a full understanding of the corrosion process for the (Th,Pu)O₂ compounds. The experiments will continue until a steady-state concentration level is reached. Moreover, the studies on unirradiated samples will be extended to irradiated „Th-MOX“.

References:

- [1] J. Bruno et al., SKB Technical Report, TR-97-33 (1997)
- [2] W.E. Falk et al., CHEMVAL 2: Thermodynamics database. EUR 16897 (1996)
- [3] R. Knopp et al., Rad. Chim. Acta 86 (1999) 101

Contact:

J. Cobos, tel.: +49 7247 951 548
joaquin.cobos.sabate@ec.europa.eu

Redox chemistry and secondary phases in Fe-Np-Pu systems

The experiment to investigate systematically redox interactions between iron canister material and ²³⁷Np and ²³⁹Pu are ongoing. Pure iron coupons, some of which preliminarily corroded under reducing conditions, are exposed to synthetic groundwater solutions containing different combinations of Np(V), Pu(V), U(VI), Tc(VII), Se(VI). The optimization of the pre-corrosion procedure of Fe has continued using various experimental configurations. The secondary phases re-precipitated onto the iron during the tests with the solutions are analyzed using SEM-EDS, SIMS, and other spectroscopy techniques, to characterize the incorporation/retention behaviour of the radionuclides. Fig. 4 shows results from SIMS analysis on iron coupons corroded during spent fuel leaching experiment and provides evidence

4. Spent Fuel Characterisation

for the incorporation of U and Pu on the corrosion layer, with Fe-Si compounds as main corrosion species. Evidence for incorporation of Np, Tc, Sr was also obtained. These results may have a significant impact on the safety assessment of a deep geologic repository under reducing conditions.

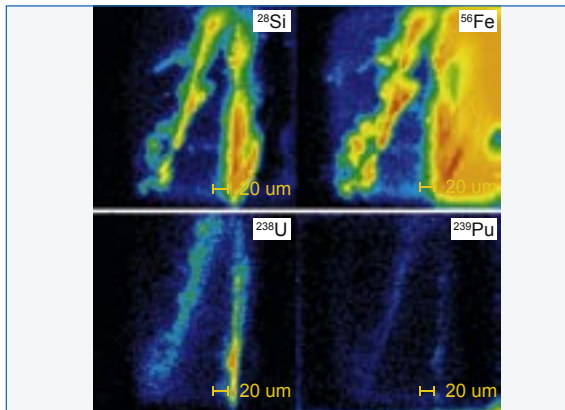


Fig. 4: SIMS analysis of corrosion layer on iron surface showing the presence of actinides in the corroded phase. The same region of a corroded iron sample was analyzed for various masses. The four images represent the result of these scans for ^{28}Si , ^{56}Fe , ^{238}U and ^{239}Pu , respectively. The bright dots/areas on each image constitute a „map“ of the nuclide presence on the analyzed surface.

Contact:

D. Cui, tel.: +49 7247 951 116
daqing.cui@ec.europa.eu

Source term studies on irradiated MOX fuel using the Knudsen cell method

An investigation to determine the grain boundary inventory for MOX fuel was started. Small fragments of ~36 GWd/t MOX fuel were annealed up to complete vaporization in a shielded Knudsen cell coupled to a quadrupole mass spectrometer. Figure 5 shows the normalized fractional release for selected fission products. Different release modes can be identified corresponding to different temperature ranges. The initial stage at temperature <1600 K can be attributed to venting of grain boundaries and cavities in the material. Although the detailed analysis of the data is still ongoing, some considerations can be made. The species showing the earliest release in this range are He, I, Te. The release up to 1500 K for these species is of the order of a few %, with smaller fractions of Cs

and Ba. The fission gas Xe is released in significant amounts at $T \sim 1500$ K, where He shows it most pronounced release peak. These values are higher than reported grain boundary inventory data from leaching experiments. This can be explained by considering the different processes (volatilization vs. water corrosion) involved in the mobilization/release of radio-nuclides. The release in the leaching experiments is linked to the fraction of grain boundary area reached by the water, whereas in the case of the annealing

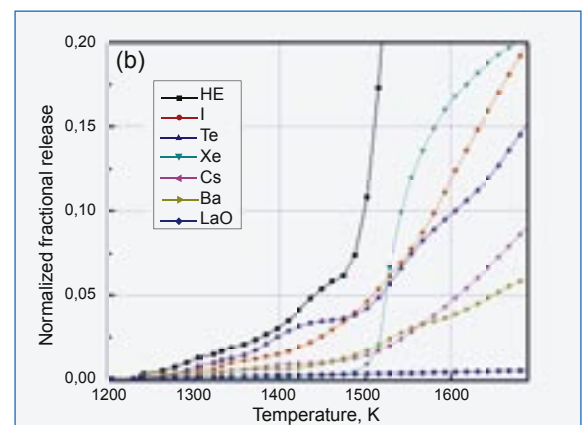
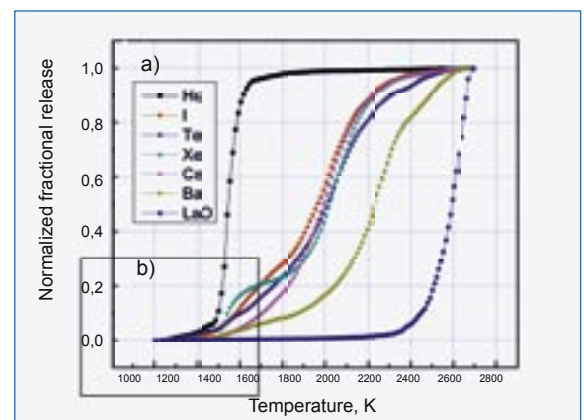


Fig. 5 (a): Normalized fractional release of selected species from irradiated MOX. The initial stages of release mainly due to venting of grain boundaries are shown in detail in inset (b).

tests all grain boundaries are affected. These results thus constitute an upper limit to assess the source term for the grain boundary component of the IRF.

Contact:

J-P. Hiernaut, tel.: +49 7247 951 385
 jean-pol.hiernaut@ec.europa.eu

V.V. Rondinella, tel.: +49 7247 951 279
 vincenzo.rondinella@ec.europa.eu

4.3 Source Term and Corrosion Studies on Irradiated Fuel

Dynamic leaching of spent fuel under oxidising conditions

Three experiments were carried out on ~67 MWd/KgU UO_2 using the experimental set-up described in the previous annual report (EUR 22105 EN - ITU Annual Report 2005 p. 45). The experiments were performed at three different flow rates, in 1 mM NaHCO_3 + 19 mM NaCl aqueous solution under oxidising conditions at room temperature. Results obtained during the reporting period show a linear response after each change of flow-rate thus demonstrating the effectiveness of the experimental set-up. As an example, the evolution of the concentration of some nuclides as a function of time is shown in Fig. 6. A convergence of the rates towards the steady state regime is reached after the initial stage of the experiment. The ratio between the individual nuclides and uranium is essentially constant. A somewhat higher level of scatter is evident for the data corresponding to the outer pellet region. The full

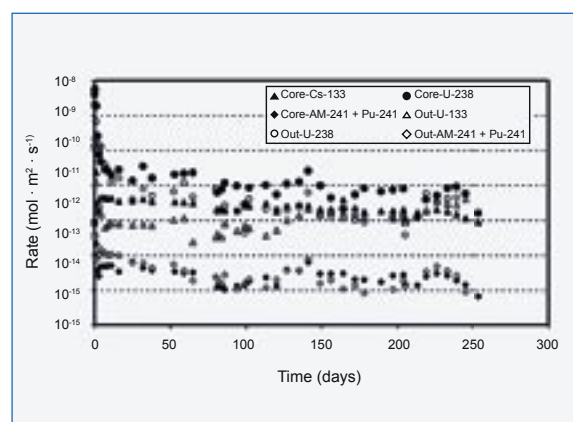


Fig. 6: Evolution of concentration with time for selected nuclides released from samples originating from the central (Core) and rim (Out) region of a fuel pellet

evaluation and interpretation of the data is ongoing. The initial release will be compared with the results obtained in static experiments carried out using the same fuel and leaching solution.

Contact:

D. Serrano-Purroy, tel.: +49 7247 951 417
 daniel.serrano-purroy@ec.europa.eu

Spent fuel rodlets in inert humid atmosphere

This study, partly in collaboration with SKB and in the framework of NF-PRO, investigates the alteration of spent fuel during the transient period following failure of a container and prior to full coverage of the fuel rod by groundwater.

Capped fuel segments containing a defect in the cladding are placed in an autoclave partly filled with water at 90°C (see Fig. 7). The test duration is sev-

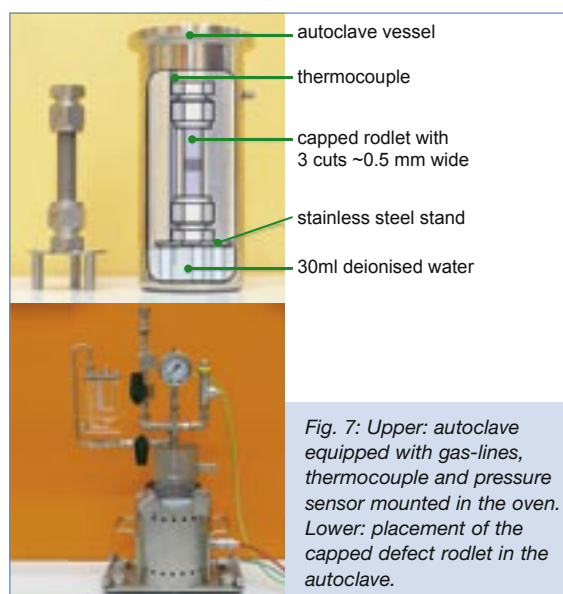


Fig. 7: Upper: autoclave equipped with gas-lines, thermocouple and pressure sensor mounted in the oven. Lower: placement of the capped defect rodlet in the autoclave.

eral months. After the test, the rodlets are examined to determine whether any alteration has occurred in the water vapour atmosphere. Furthermore the composition of the gaseous and water phases is analyzed by mass spectrometry. Different atmospheres will be used in the autoclave: argon, a mixture of argon and hydrogen, and finally hydrogen. The first experiment was carried out on a defective rodlet in humid Ar-atmosphere for 5 months: the gas pressure during

4. Spent Fuel Characterisation

the experiment increased by about 11% which can be attributed mainly to fission gas release and also to radiolytically produced hydrogen. The oxygen content in all gas samples was below the detection limit (10 ppm). SEM examination showed a slightly corroded surface near the defect.

Contact:

D. Wegen, tel.: +49 7247 951 364
detlef.wegen@ec.europa.eu

4.4 Radiation Damage and Solid State Studies

First-principles calculations of defects in nuclear fuels

ITU recently launched first-principle nuclear fuel calculations (in collaboration with the Institute of Solid State Physics (ISSP), Riga, and Imperial College, London) using the Density Functional Theory (DFT) combined with the plane wave basis set as implemented into the VASP computer code.

The work focused on defect properties of UN (as a possible nuclear fuel) in a cubic phase [1, 2]. It was shown that N vacancies very slightly affect the UN lattice constant, even for concentrations as high as 25%. The lattice response, more reminiscent of a metal rather than an ionic or semiconducting material like UO_2 , is confined to small inward displacements of the nearest neighbour uranium ions and a very local defect-induced electronic density redistribution. The relevant decrease in a supercell volume (the defect volume) is $\sim 3.5 \text{ \AA}^3$. Conversely, U vacancies induce somewhat larger defect volumes (4.75 \AA^3) which increase in magnitude as a function of defect concentration (10.58 \AA^3 at 25%). In this case the nearest neighbour nitrogen atoms are displaced outwards and the hole's charge is distributed over first and (to a lesser extent) second neighbour atoms. Unlike U and N vacancies, interstitial N atoms induce lattice expansion (defect volume 5.13 \AA^3).

Once lattice relaxation is complete, the Frenkel and Schottky pair formation energies are very similar. Consequently, intrinsic vacancies and intersti-

tial defects exist in comparable concentrations so that both are available to mediate defect transport. Analysis of the electron density redistribution shows that the effective charge of N atoms depends critically on their position and environment; this limits the applicability of standard MD simulations based on formal invariant charged species to defect studies in nitrides. The results of the calculations agree well with those obtained using the Cambridge Serial Total Energy Package (CASTEP) code [2].

The calculations of N vacancies on the UN (001) surface indicated an 8% decrease of the formation energy, compared to the bulk. This indicates that vacancies would segregate to the grain boundaries.

[1] E.A. Kotomin et al., Phys. Status Solidi C (2007) 1193

[2] E.A. Kotomin et al., J Phys. Condens. Mat. 19 (2007) 106208

Contact:

E. Kotomin, tel.: +49 7247 951 445
eugene.kotomin@ec.europa.eu

Growth mechanisms of interstitial loops in α -doped UO_2

A new model has been developed [1] to simulate the defect evolution in UO_2 sintered pellets, doped with $\sim 10 \text{ wt\% } ^{238}\text{Pu}$ and stored for 4 and 7 years. The initial set of equations proposed by Hayns [2] has been extended to the doped materials and to take into account additional phenomena, i.e. the re-solution of interstitials from the loops due to the impact with the ^{234}U recoil atom and the coalescence of diffusing dislocation loops. The latter mechanisms are known to play a role in the distribution of fission gas bubbles in irradiated UO_2 fuel, which has prompted the study of their effects on the growth mechanism of interstitial loops. A sensitivity analysis has been performed, showing the important effects of the uranium interstitial diffusion and uranium Frenkel pair recombination coefficients, whereas the range of the recoil atom has a small influence on the simulated loop size distributions. It is also shown that the re-solution and coalescence processes alone have an important and positive effect on the loop size distributions. The former enables steady-state to be reached and is in competition with a growth mechanism purely based on trapping interstitials. The latter

enables to simulate the positive skewness or „tail“ oriented towards larger loop sizes, which is typical of the present coarsening mechanism and similar to the one observed on the experimental distribution. In 2007 numerical difficulties to solve the global system, i.e. the one consisting of the re-solution and coalescence processes, will be addressed.

References:

- [1] J. Jonnet, „A contribution to the understanding of the high burn-up structure formation in nuclear fuels“, PhD, Institut National Polytechnique de Lorraine, December 2006
- [2] M.R. Hayns, J. Nucl. Mat. 56 (1975) 267

Contact:

P. Van Uffelen, tel.: +49 7247 951 384
paul.van-uffelen@ec.europa.eu

Selected Publications

- E. Heifets, E. Kotomin, A.V. Trepakov
Calculations for antiferrodistortive phase of SrTiO_3 perovskite: hybrid density functional study.
J. Phys. Condens. Mat. 18 (2006) 4845
- D. Fuks, Y. Zhukovskii, E. Kotomin, D.E. Ellis
Metal film growth on regular and defective $\text{MgO}(001)$ surface: a comparative ab initio simulation and thermodynamic study.
Surf. Science Lett. 600 (2006) L99-L104
- J. Shiue, M.J. Matthewson, P.R. Stupak, V.V. Rondinella
Effects of silica nanoparticle addition in the secondary coating of dual-coated optical fibers.
Acta Mater. 54 (2006) 2631
- A. Moeslang, T. Wiss
From fission towards fusion.
Nat. Mater. 5 (2006) 679
- J.-Y. Colle, J.-P. Hiernaut, D. Papaioannou, C. Ronchi, A. Sasahara
Fission product release in high-burn-up UO_2 oxidised to U_3O_8 .
J. Nuc. Mat. 348 (2006) 229
- J. Jonnet, B. Remy, P. Van Uffelen
Stress function determination for dislocation configurations obtained from Kroener's theory.
Theor. Appl. Fract. Mec. 45 (2006) 238
- E.S. Yakub, C. Ronchi, I.L. Iosilevski
Thermodynamic model of solid non-stoichiometric uranium dioxide.
J. Phys. Condens. Mat. 18 (2006) 1227
- T. Wiss, J.-P. Hiernaut, P.M.G. Damen, S. Lutique, R. Fromknecht, W.J. Weber
Helium behaviour in waste conditioning matrices during thermal annealing.
J. Nucl. Mater. 352 (2006) 202
- A. Ciriello, V.V. Rondinella, D. Staicu, J. Somers
Thermophysical characterization of nitrides: preliminary results.
2006 ANS Annual Meeting - Nuclear Fuels and Structural Materials for the Next Generation Nuclear Reactors,
ANS Transactions 94 (2006) 711, Reno (USA) 4-8 June 2006

- V.V. Rondinella, A. Ciriello, D. Staicu, J.-P. Hiernaut, M. Walter
Experimental studies on behaviour and properties of nitride fuels.
2006 ANS Winter Conference -, ANS Transactions 95 (2006) 183 / ISSN 0003-018X Albuquerque (USA) 12-16 November 2006
- D. Cui, V.V. Rondinella, J. Low, J. Pan, G. Tamborini, K. Spahiu
On the behaviour of spent fuel under simulated early canister-failure conditions.
2006 International High Level Radioactive Waste Management Conference, Proceedings of the Conference (2006) 925
Las Vegas (USA) 30 April - 4 May 2006

Collaborations

- Belgium:** K. Lemmens (SCK-CEN, Mol)
- Canada:** R. Verrall, Z. He (Atomic Energy of Canada AECL)
- France:** C. Corbel (Commissariat à l'Energie Atomique CEA, Orsay); C. Jegou, D. Roudil, X. Deschanel (Commissariat à l'Energie Atomique CEA, Marcoule); P. Garcia (Commissariat à l'Energie Atomique CEA, Cadarache); G. Blondiaux (CNRS, Orléans); L. Thomé (CNRS, Orsay); C. Poinssot (Commissariat à l'Energie Atomique CEA, Saclay); B. Grambow (ARMINES, Nantes); M. Perdicakis (LCPME, Univ. Nancy)
- Germany:** V. Metz, E. Bohnert, A. Loida (Forschungszentrum Karlsruhe FZK-INE); W. Bors (GSF-Forschungszentrum Institut für Strahlenbiologie, Neuherberg); W. von Lensa, J. Fachinger (Forschungszentrum Jülich FZJ)
- Hungary:** Z. Hozer (KFKI, Atomic Energy Research Institute, Budapest)
- Italy:** A. Faucitano (Univ. Pavia); F. Vettraino (Ente per le Nuove tecnologie, l'Energia e l'Ambiente ENEA, Rome); L. Luzzi (Politecnico di Milano); P. Scardi, R. Ceccato (Univ. Trento)
- Japan:** T. Kameyama, M. Kinoshita, S. Kitajima, T. Matsumura, T. Nauchi, A. Sasahara, T. Sonoda (Central Research Institute of Electric Power Industry CRIEPI)
- Latvia:** Yu. Zhukovskii, V. Kuzovkov (Institute of Solid State Physics, Riga)
- Spain:** J. Quinones (Ciemat); I. Casas, J. Pablo (Univ. Politècnica Catalunya); J. Bruno (ENVIROS, Barcelona); A. Martinez Esparza (Empresa Nacional de Residuos Radiactivos, S.A.)
- Sweden:** K. Spahiu (Swedish Nuclear Fuel and Waste Management Co.); M. Jonssons (KTH, Stockholm)
- UK:** H. Eccles, B. Dunnett, R. Short (NEXIA); K. Stephenson, M. Barker (British Nuclear Fuels BNFL); R. Grimes (Imperial College, London); J. Gavartin, A. Shluger (Univ. College, London); C. Puxley (AWE Aldermaston)
- USA:** B. Hanson, B. Weber (Pacific Northwest National Laboratory); B. Finch (US Department of Energy DOE, Washington); J. Fortner (Argonne National Laboratory); S. Conradson (Los Alamos National Laboratory); R. J. Kennedy (Idaho National Laboratory)

5. Safety of Nuclear Fuels

Highlight

High Temperature Reactor Coated Particle Fuel

The JRC-ITU pursues two activities in the frame of High Temperature Reactor (HTR) fuels. In the Hot Cell Technology Unit the safety testing of irradiated HTR fuels under loss of coolant flow in conjunction with a depressurisation of the reactor vessel is investigated. Given the strong negative reactivity coefficient of the fuel, this reactor type shuts down immediately if the temperature begins to increase. Owing to the reactor's low power density and the large thermal graphite mass within the core, a loss of coolant flow would cause the core temperature to increase to no more than 1620°C [1]. The licensing of HTR fuels requires not only a proven in-pile performance, but also an excellent behaviour in such off-normal operating conditions.

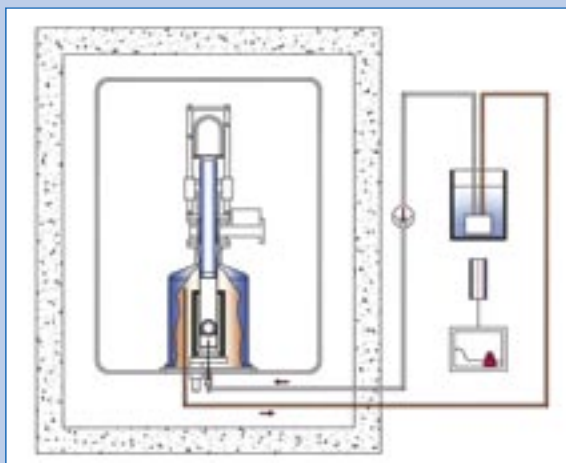


Fig. 1: Schematic representation of the KÜFA device in a Hot Cell, showing the gas circuit and gaseous fission product measurement

The installation of the KÜFA (KühlfingerApparat) device (see Fig. 1), originally developed at the Forschungszentrum Jülich, has established a world wide unique competence in the safety testing of HTR fuel at ITU. The KÜFA device consists of a high temperature ($T_{\text{max}} = 1800^{\circ}\text{C}$) furnace through which helium is swept and passed through a set of detectors to quantify gaseous fission product release. In addition to this continuous measurement facility, the device is fitted with a cold finger on which a plate (held at 70°C) is mounted to collect solid fission products, which can be released from the fuel at these high temperatures. Periodic exchange of this plate, without interruption of the heating, permits a

time dependent analysis of their release. In 2006, the commissioning of this device was completed. The results of one of the first tests on a spherical fuel element produced by NUKEM and irradiated in the HFR Petten (in the HFR – K6/3 experiment) to a burn-up of 9.7% FIMA are shown in Fig. 2. This fuel element showed excellent behaviour under these conditions and not one of the ca. 14,600 coated fuel particles in the fuel element failed in the test made at 1600°C .

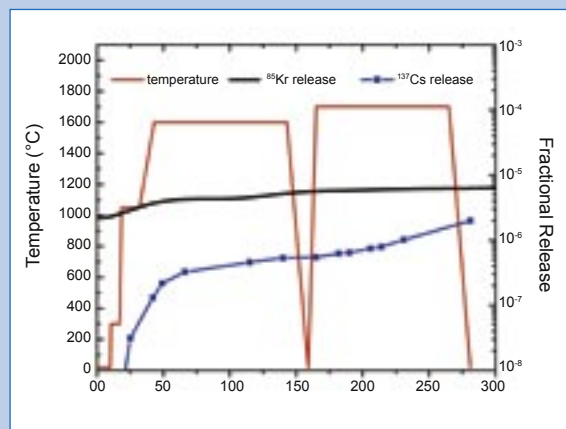


Fig. 2: Krypton and caesium released from a HTR fuel element with a burn-up of 9.7% FIMA, during heating to 1600 and 1700°C

In parallel, the Nuclear Fuels Unit is installing a facility to fabricate Pu and eventually minor actinide based coated particle fuels. The high burn-up achievable with coated particle fuel provides a real possibility to use this concept as a means to transmute Pu and minor actinides, enabling a better use of the energy resource still available in spent fuel from a fleet of light water reactors.

Novel fuel kernels and innovative routes to their production are required both to reduce waste streams and to improve fabrication safety. $(\text{Zr},\text{Y},\text{Pu})\text{O}_2$ kernels have been produced using a method based on the infiltration of porous $(\text{Zr},\text{Y})\text{O}_2$ kernels by a Pu nitrate solution [2]. Recently, $(\text{Zr},\text{Y},\text{Am})\text{O}_2$ kernels have been prepared by the same route, and 10 wt% Am incorporated in a single infiltration step (see Fig. 3). Further improvements in the process are still necessary to minimise the number of kernels with cracks and irregular shapes.

These kernels must be coated in several layers to establish the release barriers in the HTR particle fuel. This is achieved using a fluidised bed chemical vapour deposition (CVD) process (see Fig. 4). The layers are formed by the cracking of precursor gases at high temperature. The layer density and morphology is controlled by the furnace temperature and the gas flow rate. The chemical vapour deposition facility (see Fig. 5) has been designed and ordered. Within the current planning, it will be delivered in 2007 and go into operation in 2008.



Fig. 3: Optical macrograph of $(Zr,Y,Am)O_2$ kernels (Am content ca. 10 wt% and $\phi \sim 600 \mu m$) produced at ITU

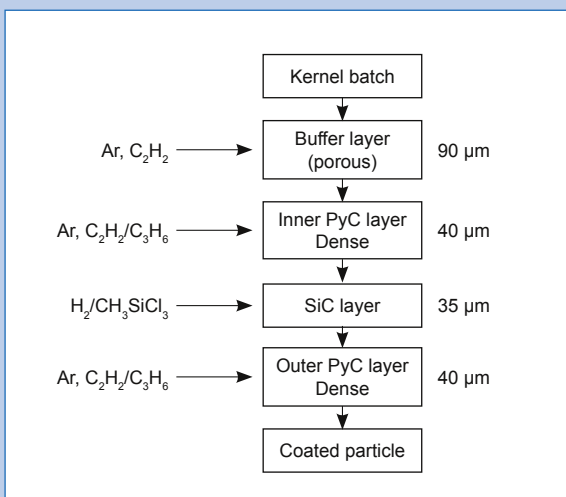


Fig. 4: The CVD process to produce HTR coated particles



Fig. 5: Impression of the CVD furnace and gas scrubbing unit for the fabrication of coated particle fuel

References:

- [1] K. Kugeler, R. Schulten, "Hochtemperaturreaktortechnik HTR", Springer (1989)
- [2] J. Somers, A. Fernandez, Progress in Nuclear Energy 48 (2006) 259

Contact:

J. Somers, tel.: +49 7247 951 359
joseph.somers@ec.europa.eu

E. Toscano, tel.: +49 7247 951 409
enrique.toscano@ec.europa.eu

5. Safety of Nuclear Fuels

5.1 E-Modulus of Uranium Oxides in the Temperature Range 20-550 °C by Instrumented Indentation

Previous measurements on non-irradiated pure and doped- UO_2 by both synchrotron compressibility and Knopp-indentation tests have shown the room-temperature elastic modulus ($E_{20^\circ\text{C}}$) of uranium dioxide to increase with the amount of dissolved elements in the matrix (simulated burn-up) [1]. This contrasts with results of Knoop-indentation and microacoustic tests in hot-cells, which show the $E_{20^\circ\text{C}}$ -values of irradiated LWR-fuels to decrease with burn-up [2]. The behaviour is due to the change of the hardness-to-modulus ratio of the material (H/E), which moves from the value ~ 0.026 in the as-sintered state, to a value of ~ 0.055 after irradiation [2]. The origin of the phenomenon still remains unexplained. In the present experiments instrumented indentations tests were applied to confirm the formerly measured elastic response of pure and doped UO_2 in the non-irradiated state. In the tests both the indentation load and the penetration depth are recorded simultaneously as function of time; the elastic response of the material is extracted from the unloading curve, e.g. by the widely used Oliver-Pharr method [3, 4]. The temperature range of the reported tests was 20-550°C. The employed device was a high temperature, instrumented indenter developed at ITU for the use in hot-cells. The maximum operation temperature of the device lies around 1300 °C.

Results of the above referred instrumented indentation tests are shown in Figs. 1 and to 2. In Fig. 1, examples of indentation curves (loading and unloading parts) for UO_2 and SIMFUEL (burn-up 8 at %) samples are shown for the temperatures 20, 300 and 550 °C at a maximum indentation load of 1000 g. For E-modulus determinations by the Oliver-Pharr method [3, 4], the main parameters of these curves are the unloading stiffness ($S = dP/dh_{\text{max}}$) and the contact depth after elastic recovery (h_c). The latter is given by $h_c = h_{\text{max}} - \varepsilon P_{\text{max}}/S$, where P_{max} and h_{max} are respectively the peak load and the maximum penetration depth, and ε is a constant that usually takes the value 0.75. According to [3, 4], for different indentation loads the equation $S^{-1} = C_m + \frac{1}{2} \pi^{1/2} E_{\text{eff}}^{-1} A_c^{-1/2}$ is fulfilled, where C_m is the machine compliance and A_c is the contact area, proportional to the contact depth (h_c) to the power 2. In this equation E_{eff} is the effective elastic modulus of the sample, satisfying $E_{\text{eff}} = (1 - \nu_{\text{spec}}^2)/E_{\text{spec}} + (1 - \nu_i^2)/E_i$, where ν_{spec} ,

ν_i and E_{spec} , E_i are respectively the Poisson's ratios and the E-values of the specimen and indenter materials. The Young modulus of the specimen (E_{spec}) is derived from the slope of the plots S^{-1} vs. $A_c^{-1/2}$, provided ν_{spec} is determined (ν_i and E_i are known data) [3, 4]. Figure 2 shows the S^{-1} vs. $A_c^{-1/2}$ plots for the UO_2 sample at 20, 300 and 550 °C for the load range 50-1500 g. The correspondingly derived E-modulus values, by assuming $\nu_{\text{spec}} \approx 0.3$, are also given in the plots.

In addition to the usual decrease of the E-modulus with temperature (increasing slopes in the plots of Fig. 2), the results show in general higher E-values for the SIMFUEL sample compared to pure UO_2 , which agrees with the results obtained at room-temperature by other techniques (non-irradiated samples) [1]. The

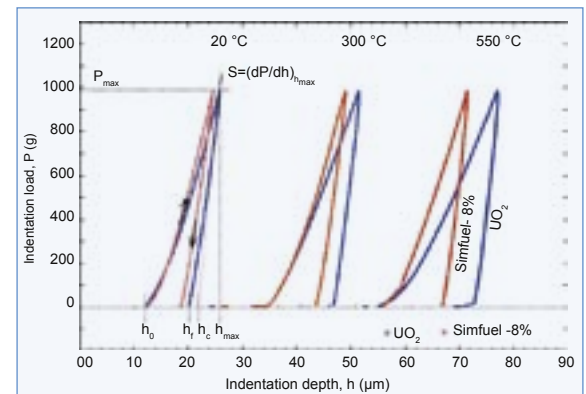


Fig. 1: Indentation load vs. penetration depth curves of UO_2 and SIMFUEL (AECL-8 %) samples at temperatures of 20, 300 and 550 °C. Vicker's diamond indenter. Nominal maximum indentation load: 1000g.

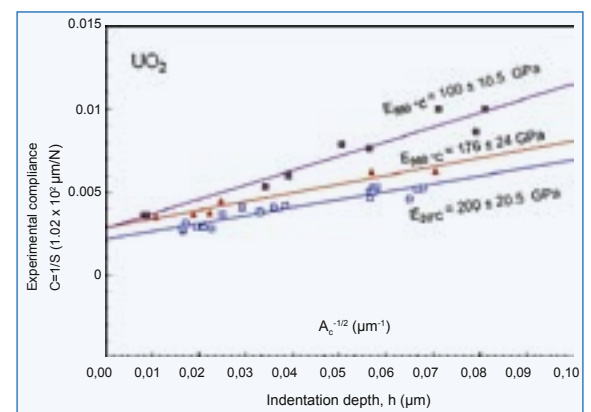


Fig. 2: Indentation E-modulus of UO_2 . Experimental compliance vs. inverse of the square root of contact area ($A_c^{1/2}$) (Oliver-Pharr method). Derived E-modulus values at 20, 300 and 550 °C and error ranges. Applied load range 50-1500 g.

presently determined E-values at room temperature, i.e., $E_{20^{\circ}\text{C}}(\text{UO}_2) = 200 \pm 20.5$ GPa and $E_{20^{\circ}\text{C}}(\text{SF-8\%}) = 343 \pm 83$ GPa are fully compatible with the values reported in [1] and with literature values of pure UO_2 . Further instrumented indentation tests are in progress to confirm the observed trends at temperatures above 550°C .

References

- [1] M. C. Pujol et al., J. Nucl. Mater. 324 (2004) 189
- [2] J. Spino et al., EUR 22105 EN - Institute for Transuranium Elements – Annual Report 2005
- [3] W.C. Oliver et al., J. Mater. Res. 7 (1992) 1564
- [4] W.C. Oliver et al., J. Mater. Res. 19 (2004) 3
- [5] J. T. A. Roberts et al., J. Nucl. Mater. 41 (1971) 23

Contact:

J. Spino, tel.: +49 7247 951 233
jose-luis.spino@ec.europa.eu

M. Ernstberger, tel.: +49 7247 290
markus.ernstberger@ec.europa.eu

5.2 Post-Irradiation Examination of High Burn-up MOX Fuel

In-pile performance studies of BNFL's SBR MOX fuel continued in 2006 with the post-irradiation examination of six rods irradiated for five cycles in the Beznau-1 PWR, Switzerland. The assembly was irradiated to an average burn-up of 49 MWd/kgHM while the lead rod achieved an average rod burn-up of around 54 MWd/kgHM, which is the highest burn-up reached to date by SBR MOX in a commercial irradiation.

During the reporting period the following examinations were performed on the rods: oxide thickness, gamma scanning, rod-length measurement, profilometry, defect determination and rod puncturing for determination of fission gas release. The results were compared with those obtained after three and four cycle irradiations. The main objective is to demonstrate the performance of SBR MOX fuels over a wide range of burnup and to provide a comprehensive picture of the fission gas behaviour.

Visual examination of the rods showed that the pellet-pellet interfaces are visible as circumferential bands on the outside of the cladding. Gamma scanning, however, did not reveal significant gaps in the fuel stacks. Moreover, no axial migration of volatile fission products, such as Cs, had occurred. All the rods exhibited an oxide layer which occasionally showed local spalling close to the regions of maximum thickness. Eddy current measurements (see Fig. 3) revealed that the peak oxide thickness is around $80\text{ }\mu\text{m}$ for the lead rod (F2), which contrasts with $45\text{ }\mu\text{m}$ from the 4-cycle measurement. The plot shows that significant growth in oxide layer thickness had occurred in the 5-cycle fuels. It is also apparent that as the burnup increases the oxide layer growth is enhanced at higher positions on the rod. This is attributed to a positive feedback mechanism whereby as oxide thickness increases the thermal conductance of the oxide layer is reduced. It results in an increased metal-oxide interface temperature leading to increased corrosion rates which produce both a sharply peaked oxide profile and an increase in oxide growth rate.

Profilometry measurements showed that the rods with the highest burnup and power ratings have the largest diameters. On 3- and 4-cycle fuels it was observed that after the fuel had densified and the clad had crept down in early irradiation, solid-fission product swelling began to increase the fuel-stack diameter, and expand the cladding. However, for the 5-cycle fuel, the clad diameter remained below the as-fabricated diameter (10.65 mm compared with the 10.72 mm as-fabricated diameter).

Puncture results from the 5-cycle rods are shown in Fig. 4. In the plot, results from 2- 3- and 4-cycle MOX have been added along with comparison measurements for MIMAS commercial MOX, and UO_2 . Fission gas release in SBR MOX is found to be generally less than in other fuels. Fuel swelling and ceramography results from ramp testing of 3-cycle SBR MOX have demonstrated its ability to retain gas on grain boundaries. Fission gas swelling may actually be beneficial in promoting oblate rather than cylindrical pellet shapes and therefore reducing pellet clad interaction (PCI) at pellet edges.

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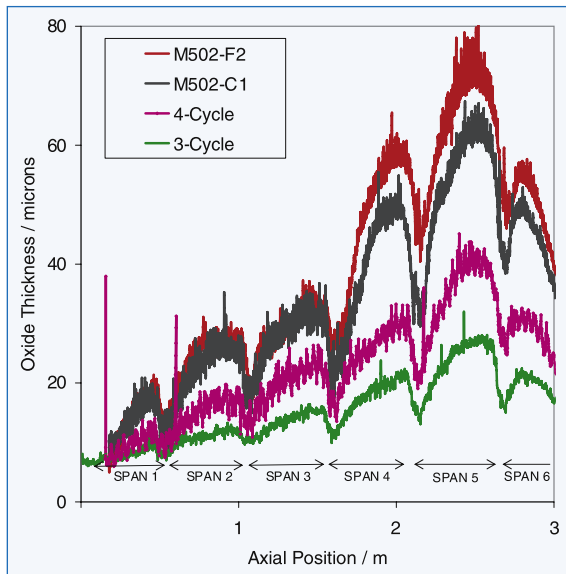


Fig. 3: Oxide thickness on BNFL SBR MOX rods showing significant growth in oxide thickness on lengthening the irradiation time from 3-cycles to 5-cycles

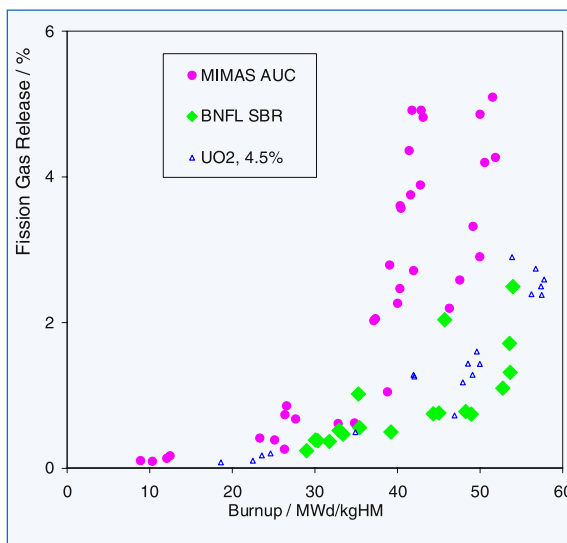


Fig. 4: Fission gas release from BNFL SBR MOX, MIMAS AUC MOX and UO_2

References

- [1] M.A. Barker et al., TOPFUEL 2006 - International Meeting on LWR Fuel Performance. Salamanca (Spain) 22-26 October 2006

Contact:

S. Brémier, tel.: +49 7247 951 556
stephane.bremier@ec.europa.eu

M. Ernstberger, tel.: +49 7247 290
markus.ernstberger@ec.europa.eu

5.3 Phébus Fission Product (FP) Post Irradiation Examination

ITU continues its involvement in the Phébus FP international reactor accident project. The FPT2 test was performed under low steam flow conditions to simulate the reducing conditions that could occur with large H_2 production. In the tests, a 20 x 1m-rod bundle of irradiated fuel (burn-up: ~35 MWd/kgU) was overheated and allowed to degrade and release the fission products, which were captured downstream in an instrumented, simulated primary circuit. The previous FPT1 test used an irradiated fuel under full steam flow. Following the sectioning of the FPT2 bundle into 2 cm discs from key sections of the bundle, ITU continued the examination by low and high power optical microscopy in the Hot Cells Technology Unit. In the previous year the electron microprobe analysis (EPMA) results from the section at the corium pool level (Disc 4) and below the corium pool (Disc 2) were reported. In 2006, Disc 1 located 41.5 mm below the bottom of the fuel column was examined by optical microscopy and EPMA. It was noted that FPT2 had

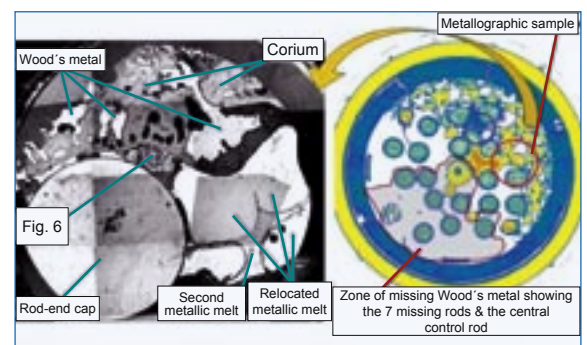


Fig. 5: Microscopic sample extracted by coring from the upper surface of Disc 1 (Mag. ~8x) along with its position on the X-ray tomography at the axial location of the disc. The rod-end plug is seen along with metallic melts at the top and ceramic melted material at the bottom of the section.

as in previous tests (FPT0 & 1) a central cavity above a melted pool of corium. The cavity in FPT2 was larger and the corium pool deeper than in FPT1 since the FPT2 bundle spent considerably longer time at full power than FPT1. There was also material that had relocated to below the bottom of the bundle, which was one of the reasons to examine Disc 1 at this very low position.

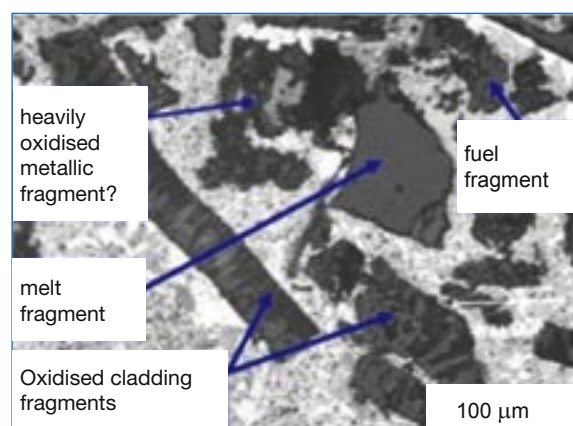


Fig. 6: Ceramic fragment of oxidised cladding, degraded metallic pieces and fuel embedded in Wood's metal (Mag. 210x)

The microscopic sample extracted from Disc 1 is seen in Fig. 5 and shows the Zircaloy end-plug of a fuel rod as well as large slugs of bright lustrous metal, which is most likely to be silver from a melted absorber rod. In between the absorber melt another, less bright melt phase is noted: this is probably to be melted structural materials since it contains Zr and Fe. It is also likely to contain Ni although a complete analysis was not carried out. The remaining areas were corium with debris in the embedding material (Wood's metal). The debris included fragments of what appeared to be oxidised structural material and pieces of oxidised cladding and fuel. A higher power micrograph is shown in Fig. 6 of a central region of debris in between the end-plug and the corium (see Fig. 5 for location). It can be seen that the corium is a single phase ceramic (with possibly small amounts of secondary phases at grain boundaries). It was analysed at a number of points and two zones were identified: one slightly richer in U and the other slightly richer in Zr. The latter was presumed to have interacted less (assuming the initial liquid is melted Zircaloy) and appeared to have arrived later. X-ray maps also indicate in some instances local differences in composition. Thus adjacent grains may exhibit noticeable

variations in their U and Zr contents. Possibly the cooling has been sufficiently rapid to 'freeze in' the inhomogeneous elemental distribution. There is a low Fe content; the iron is also seen to segregate slightly towards the boundaries in these grains. The overall the corium composition is close to the typical corium of the pool of about $(U_{0.5}Zr_{0.5})O_2$.

Contact:

D. Bottomley, tel.: +49 7247 951 364
paul.bottomley@ec.europa.eu

5.4. Bulk Nanocrystalline/ Microporous ZrO_2 -Ceramics Simulating the Rim-material

The characterization of the High Burn-up Structure (HBS) of LWR fuels is usually restricted to microscopic or sub-microscopic observations. Investigations of bulk properties of the material often fail because of difficulties in preparing appropriate large specimens for the performance of standard tests. To partially overcome these difficulties, a programme has been launched for the production and properties measurement of bulk-homogeneous samples, based on ZrO_2 -ceramics with a tailored microstructure resembling that of the HBS. The aim is to study the influence of the pore/grain morphology on both mechanical and thermal properties. Examples of the achieved microstructure in 25 mm-discs of 4% Y_2O_3 - ZrO_2 were presented in [1], showing the close similarity of the surrogate material to the target microstructure (rim HBS). In the present communication preliminary results from uniaxial compression tests carried out on the material are reported. Figure 7 shows the test configuration and both macrograph and high magnification micrograph of the specimen tested.

Typical of the HBS, the specimen of Fig. 7 was provided with an initial porosity of 12 %, constituted essentially of quasi-spherical $\sim 1 \mu m$ - diameter pores. The initial grain size was ~ 200 nm. The test temperature was 1200 °C; the compression stress applied was ~ 585 MPa, i.e., somewhat in excess of that in the reactor. Owing to the high stress applied, the 1 cm thick Al_2O_3 wafers used to separate the specimen

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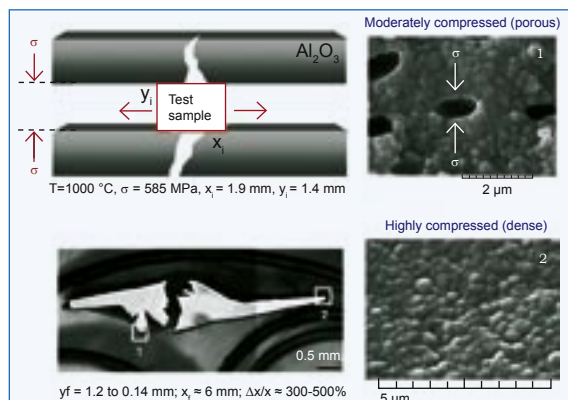


Fig. 7: Results of a compression test on nanocrystalline/porous 4%Y₂O₃-ZrO₂ (dummy rim-material) at 1200 °C. Initial specimen dimensions (mm): 20 x 1.9 x 1.4. Maximum load applied: 585 MPa; load speed 146 MPa/min; hold-time at maximum load 2 h.

from the machine punches fractured. The test-specimen, however, showed ductile behaviour and flowed partly into the fractures in the Al₂O₃ wafers, but mostly into the space left between the wafers, in the direction perpendicular to the stress applied. In this direction the deformation was ~300 to ~500 %, i.e., clearly in the super-plastic range. High-magnification micrographs of both the partially deformed and the highly deformed regions of the sample showed, respectively, compressed (elliptical) pores (see Fig. 7, top-right), and, moreover, fully compacted material with 100 % pore closure, with no signs of local fracture (see Fig. 7, bottom-right). Closer inspection of the grain structure after the test showed equiaxed, non-deformed grains throughout the whole specimen. The latter suggests that the observed plasticity was driven by grain-boundary-sliding. This mechanism of deformation, typical of nanocrystalline solids [2], is expected to predominate also in the HBS, favouring a more ductile behaviour compared with large grain UO₂.

Contact:

J. Spino, tel.: +49 7247 951 233
jose-luis.spino@ec.europa.eu

H. Santa Cruz, tel.: +49 7247 951 377
hernan.santa-cruz@ec.europa.eu

References

- [1] J. Spino et al., EUR 22105 EN - Institute for Transuranium Elements – Annual Report 2005
- [2] U. Betz et al., J. Mater. Sci. 36 (2001) 5811

5.5 Thermal Diffusivity of Homogeneous MOX Fuel with a Burn-up of 35 MWd/kgHM

This section describes some recent results obtained in the framework of the first commercial irradiation of British Nuclear Fuel SBR MOX fuel that took place over the period 1994–1997 in assembly M501 of the Beznau-1 PWR, Switzerland. MOX fuel rod with burn-ups in the range 31–36 MWd/kgHM was taken for post-irradiation examination at ITU. In previous publications [1, 2] the microstructure and fission gas release characterization results were described. Here, thermal diffusivity measurements are reported.

The thermal diffusivity measurements were carried out using a shielded „laser-flash“ device, designed and constructed at ITU for highly γ -active materials [3]. The samples were disc fragments, with a thickness of about 1 mm, and with lateral dimensions of the order of 3 to 5 mm. These samples are obtained by cutting discs from fuel segments, using a double blade device to ensure parallel faces. Pictures are made of the two faces of the disc in order to obtain information of the distribution of the cracks. The fuel is slowly pushed out of the cladding, and fragments are obtained after this operation. The position and orientation of the fragments used for the measurement were determined precisely. The faces were checked to be plane and parallel, without cracks. The local thermal diffusivity was measured at different radial positions by moving the pyrometer field-stop aperture (500 μ m radius) by step motors across the optical image of the specimen surface produced by a macro-objective. The thermogram for each measurement was carefully inspected to ensure that heat transfer conditions were standard. The presence of perturbations due to internal defects, such as voids and cracks, could be unambiguously detected.

Starting at about 250 °C, six thermal diffusivity measurement cycles were completed, with increasing maximum temperature up to 1000 °C. Annealing could be performed at temperatures much higher than the local

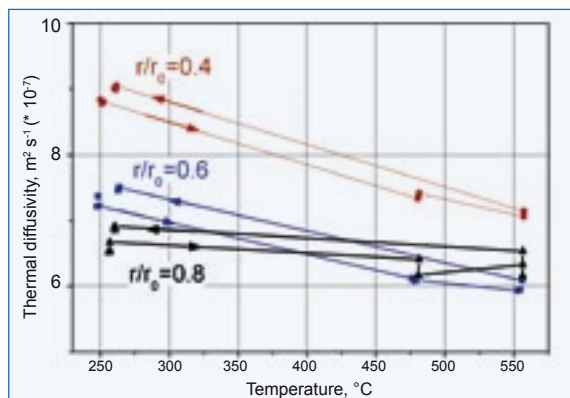


Fig. 8: Thermal diffusivity of homogeneous SBR MOX fuel with burn-up of 35 MWd/kgHM during the third measurement cycle. Measurements were made at three radial positions and temperatures of 250, 480 and 560°C, and finally again at 250°C.

irradiation temperature as the sample was particularly resistant to fracture. At each investigated temperature, the thermal diffusivity dependence on the radial position was quantified by making measurements at the three relative radial positions $r/r_0 = 0.8$, 0.6 and 0.4. Fig. 8 shows the results from the third measurement run. It can be seen that the thermal diffusivity increases from the pellet periphery to the centre. It is also seen that after the annealing cycle, a recovery of the thermal diffusivity is observed over the whole fuel radius. The measured radial profile of the thermal diffusivity and its variation during annealing can be interpreted in terms of local parameters (burn-up, irradiation temperature, auto-irradiation effects, porosity) based on a previously constructed correlation function for irradiated UO_2 fuel [4]. Comparison shows that the thermal conductivity of SBR MOX fuel is in the same range for UO_2 of similar burn-up.

References

- [1] R.J. White et al., J. Nucl. Mater. 288 (2001) 43
- [2] S.B. Fisher et al., J. Nucl. Mater. 306 (2002) 153
- [3] M. Sheindlin et al., Rev. Scient. Instr. 69 (1998) 1426
- [4] C. Ronchi et al., J. Nucl. Mater. 327 (2004) 58

Contact:

D. Staicu, tel.: +49 7247 951 263
dragos.staicu@ec.europa.eu

5.6 Nuclear Fuel Modelling

A new release of the TRANSURANUS fuel performance code

In order to simplify code management and the interface between codes, and to take advantage of hardware development it is necessary to generate one code that can cope with both normal operation and design basis accident conditions. The TRANSURANUS fuel performance code was designed from its inception in 1973 to be able to cope with normal, off-normal and accident operating conditions. Nevertheless, the extension of the application range of the code to design basis accident (DBA) conditions such as a loss of coolant accident (LOCA) required the development and implementation of specific models. The recent code version includes new Zry-4 and Zr1%Nb-specific models for high temperature oxidation, the $\alpha \rightarrow \beta$ phase transformation, plastic deformation and failure of the fuel cladding under LOCA conditions. New correlations were developed for Zr1% Nb cladding alloys that consider the inter-dependence of cladding oxidation, strain rate and mechanical strength. The new and extended version of the TRANSURANUS code was

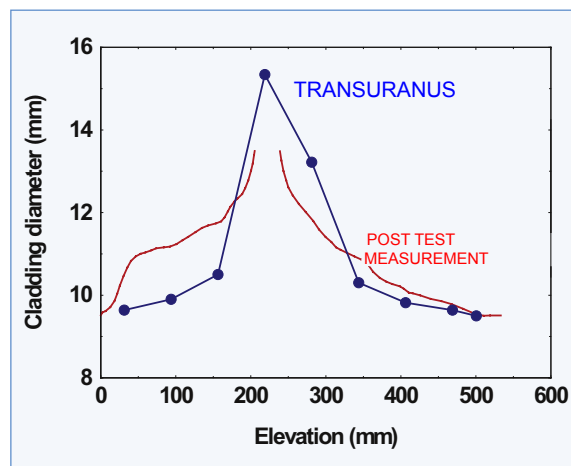


Fig. 9: Cladding deformation profiles measured after a Halden LOCA test and calculated by the TRANSURANUS code

transmitted to the user community in 2006, after having been validated on the basis of post-test analyses of numerous cladding burst experiments. These analyses proved the reliability of the code predictions for both PWR and VVER fuel rod performance in the temperature range of 600 – 1200 °C [1, 2].

5. Safety of Nuclear Fuels

Simulations of the Halden LOCA experiments in an OECD benchmark programme have also confirmed the applicability of the code to DBA analyses (Fig. 9). However, some further harmonisation of the Zry-4 and Zr1%Nb-specific models concerning the strain rate and the failure stress in the $\alpha \rightarrow \beta$ phase transition range is envisaged for the consistent simulation of the different claddings. Furthermore, experiments for measuring the temperature shift of the phase change when varying the heating rate are underway in order to model the phase change in different cladding materials for Western and Russian type reactors with a dynamic model in a consistent manner. These refinements will be further tested against the experimental results of an integral LOCA test with a VVER fuel rod in the OECD Halden Reactor, as well as the experimental data available through the FUMEX-II exercise of the IAEA and the IFPE database of the NEA.

References

- [1] P. Van Uffelen et al., Proceedings of the International Conference "Advances in Nuclear Materials: Processing, Performance and Phenomena", Mumbai (India), 12-16 December 2006
- [2] C. Györi et al., Proceedings of the KTG Technical Expert Meeting on "Status of LWR Fuel Development and Design Methods", Dresden (Germany), 2-3 March 2006

Contact:

P. Van Uffelen, tel.: +49 7247 951 384
paul.van-uffelen@ec.europa.eu

Selected Publications

- J.Y. Colle, J.P. Hiernaut, D. Papaioannou, C. Ronchi, A. Sasahara
Fission product release in high burn-up UO_2 oxidised to U_3O_8 .
J. Nucl. Mater. 348 (2006) 229
- C.T. Walker, D. Staicu, M. Sheindlin, D. Papaioannou, W. Goll, F. Sontheimer
On the thermal conductivity of UO_2 nuclear fuel at a high burn-up of around 100 MWd/kgHM.
J. Nucl. Mater. 350 (2006) 39
- S.V. Bechta, V. B. Khabensky, S.A. Vitol, E.V. Krushinov, V.S. Granovsky, D.B. Lopukh, V.V. Gusarov, A.P. Martinov, G. Fieg, W. Tromm, P.D.W. Bottomley, H. Tuomisto
Corrosion of vessel steel during its interaction with molten corium.
Nucl. Eng. Des. 236 (2006) 1810 [part 1], 1362 [part 2]
- J. Spino, A.D. Stalios, H. Santa Cruz, D. Baron

Stereological evolution of the RIM structure in PWR fuels at prolonged irradiation: dependencies with burn-up and temperature.
J. Nucl. Mater. 354 (2006) 66

S. Bremier, R. Hasnaoui, S. Portier, O. Bildstein, C.T. Walker
Installation of a shielded secondary ion mass spectrometer for the analysis of irradiated nuclear fuels.
Microchim. Acta 155 (2006) 113

P. Van Uffelen, Cs. Györi, A. Schubert, J. van de Laar, Z. Hozer, G. Spykman
Extending the application range of a fuel performance code from normal operating to design basis accident conditions.
Proceedings of the International Conference "Advances in Nuclear Materials: Processing, Performance and Phenomena", Mumbai (India), 12-16 December 2006

P. Van Uffelen
Modelling of Nuclear Fuel Behaviour
EUR 22321 EN (2006)

Collaborations

- Argentina:** A. Caneiro (Argentinean Atomic Energy Commission, Atomic Centre Bariloche)
- Armenia:** S. Azatyan (Armenian Nuclear Power Plant, Metsamor); S. Bznuni (Armenian Nuclear Regulatory Authority, Yerevan)
- Austria:** V. Inozemtsev, J. Killeen (International Atomic Energy Agency IAEA, Vienna)
- Belgium:** M. Lippens, D. Boulanger, S. CIAV, G. Toury (Belgonucléaire, Brussels); P. D'Hondt, M. Verwerf, V. Sobolev, S. Lemehev, B. Verboomen, W. Haecck (Studiecentrum voor Kernenergie - Centre d'étude de l'Energie Nucléaire SCK-CEN, Mol)
- Bulgaria:** D. Elenkov (Nuclear Regulatory Agency, Sofia); J. Stamenov (Bulgarian National Nuclear Research Centre, INRNE); V. Kalkandjiev (Sofia Univ.); R. Ivanov (Technical Univ. Sofia); J. Kostadinov (Kozloduy Nuclear Power Plant)
- Czech Republic:** F. Pazdera, M. Valach, I. Uhlir (Nuclear Research Institute, Rez); A. Miasnikov (State Office for Nuclear Safety, Prague)
- Finland:** A. Auvinen (VTT Energy Aerosol Technology)
- France:** P. Giordano, B. Adroguer, M. Barrachin, L. Desgranges, J. Lamontagne, M. Phelip, F. Charollais, J.-M. Gatt, P. Garcia, J.-P. Ottaviani, M. Chaunvin, P. Martin, J. Rouault, C. Poette, J.-M. Bonnet, G. Ducros, C. Journeau, L. Caillot (Commissariat à l'Energie Atomique CEA, Cadarache); D. Warin, (CEA, Saclay); O. Dugne (CEA, Pierrelatte); G. Harbonnier (CERCA, Romans-sur-Isère); D. Baron, R. Masson, S. Marguet, Y. Dutheillet (Electricité de France, Paris); P. Blanpain, C. Garnier, P. Guillermer, H. Segura, D. Hittner (FRAMATOME ANP SAS, Paris); A.-C. Gregoire, S. Schlutig, M. Kissane (Institut de Radioprotection et de Sureté Nucléaire, Cadarache); J. Attal (LAIN, Univ.Montpellier II);

	E. Sartori (OECD Nuclear Energy Agency, AEN-NEA, Paris); B. Remy, A. Degiovanni (Institut National Polytechn. de Lorraine INPL, Nancy); R. Zeyen, Ph. Raison (EC-JRC-IE (Phebus))
Germany:	M. Steinbrück, A. Miassödov, W. Tromm, J. Stuckert (Forschungszentrum Karlsruhe); A. Seibold, F. Sontheimer, W. Goll (FRAMATOME ANP GmbH, Erlangen); D. Sommer (Kraftwerk Obrigheim); H. Märtens, D. Bour (Techn. Überwachungsverein e.V., Hannover/Sachsen-Anhalt); J. F. Schriek, A. Iwanski (Techn. Überwachungsverein Norddeutschland e.V., Hamburg); G. Sauer (Techn. Überwachungsverein Süddeutschland e.V., München); I. Brestrich (Techn. Überwachungsverein Südwest e.V., Mannheim); H. Nabiekel, H. Werner, W. von Lensa (Forschungszentrum Jülich); R. Zipper (Gesellschaft für Reaktorsicherheit, Köln); G. Grathwohl (Keramische Brennstoffe und Bauteile, Univ. Bremen); B. Hochstein (Institut Mechanische Verfahrenstechnik und Mechanik, Univ. Karlsruhe)
Hungary:	Z. Hózer (Atomic Energy Research Institute, Budapest)
Italy:	F. Vettraino, G. Gherardi, R. Calabrese (Ente per le Nuove tecnologie, l'Energia e l'Ambiente ENEA, Bologna)
Japan:	K. Fukuda, T. Ogawa; Y. Arai (Japan Atomic Energy Research Institute JAERI, Tokai Mura)
Kazakhstan:	V. Zhdanov (NNC)
Korea:	H. S. Park (Korean Atomic Energy Research Institute)
Latvia:	A. Sternberg (Institute of Solid State Physics, Riga)
Netherlands:	R. Schram, K. Bakker (Nuclear Research and Consultancy Group, Petten); K. Müller (EC-JRC-IE, Petten)
Norway:	E. Kolstad, W. Wiesenack, Terje Tverberg (Organisation for Economic Co-operation and Development OECD Halden Reactor Project)
Poland:	M. Szuta (Institute of Atomic Energy, Otwock/Swierk)
Romania:	A. Paraschiv (Institute for Nuclear Research, Pitesti)
Russia:	V. Novikov, G. Khostov (Bochvar State Inst. for Inorganic Materials, Moscow); L. Tocheny (International Science and Technology Center ISTC, Moscow); M. Veschchunov, V. Strizhov (Nuclear Safety Institute IBRAE, Moscow); V. Khabensky, S. Bechta, V. Granovsky (NITI, St. Petersburg); A. Goryachev, V. Smirnov (RIAR, Dmitrovgrad); N. Parshin, V. Nalivaev (Research & Production Association LUCH, Podolsk); V. Bezlepki, Y. Leontiev (ATOMENERGOPROEKT SPAEP); S. Bogatov, E. Pazukhin (Kurchatov Inst. Moscow)
Slovak Republic:	M. Cvan (Nuclear Power Plant Research Institute, Trnava)
Spain:	L. Herranz (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas CIEMAT, Madrid)
Switzerland:	Ch. Hellwig, A. Nordstrøm, D. Gavillet, Z. Kopatic, T. Haste, J. Birchley, S. Gunthay (Paul Scherrer Institut, Villigen and Würenlingen)
Ukraine:	E. Yakub (Odessa State Univ.)
UK:	M. Barker T. Abram, G. Marsh, D. Every (British Nuclear Fuels BNFL, Sellafield); J. Turnbull (Independent Consultant); C. Mitchell (NNC, Cheshire); R. Grimes (Imperial College, London)
USA:	J. Rest, G. L. Hofman, M. Meyer (Idaho National Laboratory); S. Yagnik, R. Yang (Electric Power Institute); L. Ott, J. Hunn, D. Williams, G. Jellison (Oak Ridge National Laboratory ORNL, Tennessee); D. Olander (Univ. California, Berkeley)

6. Partitioning and Transmutation

Highlight

Thermal Properties of Cermet Fuels

The development of fuels and targets for transmutation of actinides is one of the most important issues in the proposed P&T concepts. Different requirements for the fuel and target design can be defined, depending on the fuel cycle strategy. For example, with multiple recycling and use of fast reactors, the high fissile content and the possibility to reprocess the fuel are of key importance. In contrast, in a once-through scenario, the stability of the material at high burn-up and as spent material for geological disposal is crucial. As the extent of transmutation must be as high as possible, the development of inert matrix fuels is a promising approach in this context. Thus, uranium-free fuels could burn plutonium more efficiently since the source of new Pu that is produced by activation of ^{238}U is eliminated. Since the transmutation process is essentially based on fissioning of actinides, a high burn-up of the fuel/target is required to reach high efficiency. This will lead to high demands on the performance of the fuel in view of the concomitant high fission-gas and helium production, fuel swelling, and chemical and mechanical fuel cladding interaction. All of these will exceed the levels at which the behaviour of existing fast reactor fuels is known. Dispersions of actinide oxides in a ceramic (cercer) or metallic (cermet) uranium-free matrix are considered as fuels for the transmutation of americium. The main advantage of such fuels compared to a solid solution is that it potentially minimizes irradiation-induced property changes in the fuel by localizing the fission damage in a limited geometric domain within the fuel. The cermet fuel offers further advantages such as, its ability to retain fission gases, volatile fission products and helium in the fuel, and its high thermal conductivity.

The performance of these innovative fuels, which have direct impact on the reactor design and transmutation performances, is largely unknown because of the lack of knowledge of their in-pile behaviour (e.g. swelling, gas release, restructuring, volatile species redistribution, corrosion) and their thermal, chemical and mechanical properties. At ITU main efforts are concentrated on developing advanced fabrication processes for these fuels and their characterization. The fabrication of composite pellets is considerably more difficult than solid solution oxide pellets.

In 2006, two Mo based cermet fuels containing either $(\text{Pu},\text{Am})\text{O}_{2-x}$ or $(\text{Pu},\text{Am},\text{Zr})\text{O}_{2-x}$ have been fabricated following a process developed at ITU [1]. The irradiation tests will be performed in the High Flux Reactor in Petten and in the Phénix reactor in Marcoule in the frame of the EUROTRANS project. In order to assess their in-pile safety, series of characterisations are needed to predict their performance under irradiation. The microstructure and physical properties of these materials have been characterised extensively by standard analytical techniques, for instance in order to demonstrate the homogeneous distribution of the fissile material in the matrix (see Fig. 1) or the chemical compatibility of the fuel with the coolant (sodium). The unique high-temperature techniques available at ITU were used to determine the heat capacity, thermal diffusivity, melting point, and stability of the fuels.

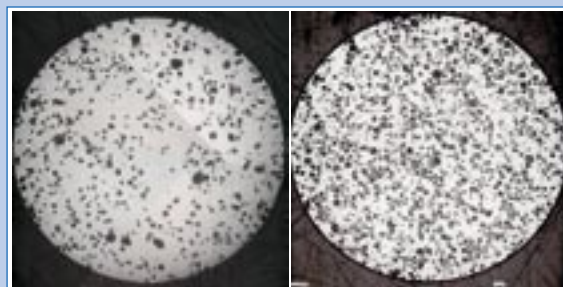


Fig. 1: Radial ceramographs of a 10%vol $(\text{PuAm})\text{O}_{2-x}$ -Mo (left) and a 40%vol $(\text{PuAmZr})\text{O}_{2-x}$ -Mo (right) cermet pellets

The thermal conductivity of the cermet fuels was deduced from thermal diffusivity and specific heat measurements. As expected, the thermal conductivity of the target is very high. Even for a volume fraction of 40% of inclusions, it is about 10 times higher than the thermal conductivity of cercer fuels with MgO matrix and with similar content of americium [2] (see Fig. 2). As a result, the operating temperature of the cermet fuels will be lower. This property allows the insertion of a larger amount of actinides in the target, without increasing significantly its temperature in pile. The high temperature stability of the fuels has been studied using a Knudsen cell combined with a mass spectrometer in the range 300 to 2800 K. The vaporisation behaviour of all the isotopes of Pu, Am, Np, Zr, Mo, the oxides (M , MO , MO_2 , MO_3), and oxygen (O , O_2) was characterised. The mass signals obtained for a cermet containing 40% volumic

fraction of $(\text{Pu}_{0.23}\text{Am}_{0.25}\text{Zr}_{0.52})\text{O}_2$ are shown in Fig. 3. A discontinuity of the signals appears around 2500 K, likely due to the melting of the ceramic part of the sample. The slow down of the vaporisation rate at 2550K is probably due to the complete evaporation of the ceramic particles at the outer surface of the sample, further vaporisation being limited by the low vapour pressure of the Mo matrix. ZrO_x vaporises mainly as ZrO at $T > 2200$ K. Molybdenum was released at $T > 2300$ K as element, none of its oxides has been detected. These results confirm the high quality of the samples, in particular the absence of significant vaporisation in the temperature range corresponding to in-pile conditions. If some oxygen would have been present during the sintering process, the Mo matrix would have been partly oxidised and would begin to vaporise at much lower temperatures (1600 K) as Mo, MoO , MoO_2 and MoO_3 . This process would liberate oxygen and therefore enhance the vaporisation of the actinide oxides. The partial vapour pressure and the enthalpy of vaporisation of all the species has been calculated from these measurements and are in good agreement with the thermodynamic predictions [3].

References

- [1] A. Fernandez et al., Actinide and Fission Product Partitioning & Transmutation. 9th Information Exchange Meeting OECD/NEA, Nîmes (France) 25-29 Sept 2006
- [2] D. Staicu et al., Measurement of thermophysical properties of the inert matrix fuels $(\text{Zr,Pu,Am})\text{O}_2 + \text{Mo}$, $(\text{Zr,Pu,Am})\text{O}_2 + \text{MgO}$, $(\text{Pu,Am})\text{O}_2 + \text{MgO}$. JRC-ITU-TN-2006/59

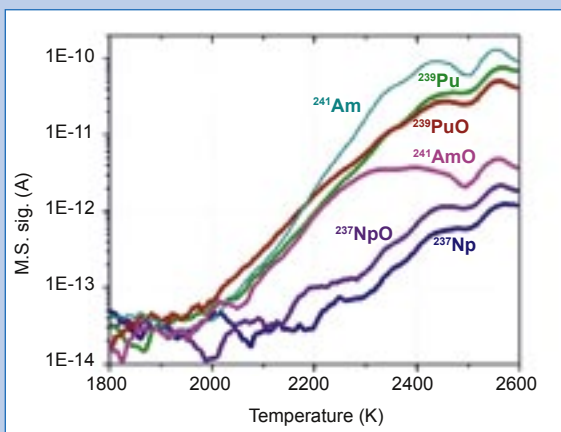


Fig. 3: Mass spectrometer signals obtained from a Mo 60%vol + $(\text{Pu}_{0.23}\text{Am}_{0.25}\text{Zr}_{0.52})\text{O}_2$ sample

- [3] J.P. Hiernaut et al., Proceedings of the International Information Exchange Meeting on Thermodynamics of Nuclear Fuels, CEA-Saclay (France) 27 Nov -1 Dec 2006

Contact:

A. Fernandez-Carretero, tel.: +49 7247 951 246
asuncion.fernandez-carretero@ec.europa.eu

J.P. Hiernaut, tel.: +49 7247 951 385
jean-pol.hiernaut@ec.europa.eu

D. Staicu, tel.: +49 7247 951 263
dragos.staicu@ec.europa.eu

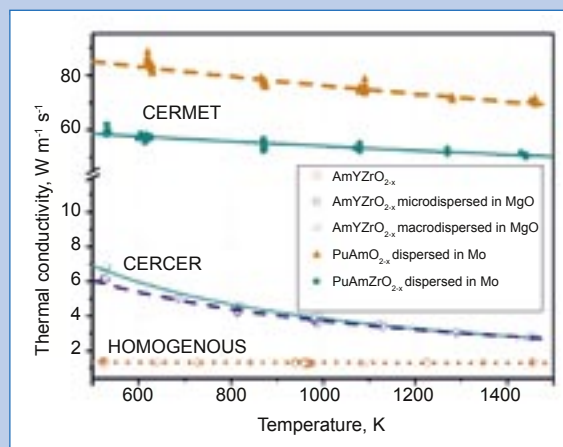
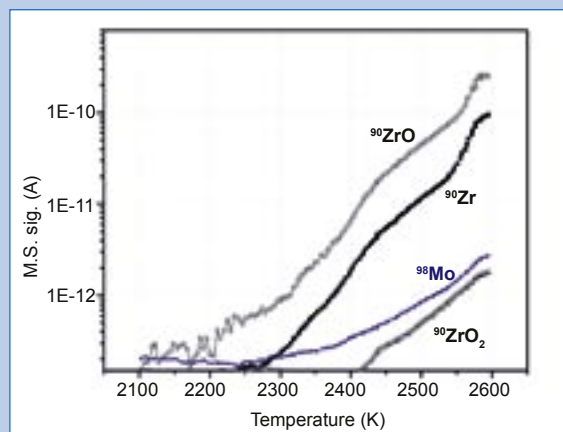


Fig. 2: Thermal conductivity of americium containing fuels: HOMOGENOUS, CERCER and CERMET fuels



6. Partitioning and Transmutation

6.1 Advanced Nuclear Studies

Through interactions between ultra-high intensity lasers and matter, it is possible to produce and accelerate electrons and protons to sufficiently high energies in order to induce nuclear reactions. Today, the fact that such lasers are compact and relatively inexpensive has led to interest in their utilization in a variety of applications, including transmutation of nuclides which are important in the nuclear fuel cycle or in medical applications such as alpha immunotherapy. Both these activities are integral to the current scientific program of ITU.

In the past year, research has continued in this field, with the primary focus on studies of photonuclear reactions at the CEA Saclay UHI-10 laser. This work has involved large collaboration with CEA (Saclay), JRC-IRMM (Geel), LULI (Ecole Polytechnique), CNR (Pisa) and Imperial College (London).

Following initial commissioning of the UHI-10 facility for work on nuclear applications, the main body of this research is now focused on electron acceleration in gas-jet targets, involving both electromagnetic and plasma (wakefield) acceleration mechanisms. High energy photon radiation fields in the form of bremsstrahlung radiation, produced from the high energy electrons, can then be used to induce reactions on suitable radionuclides of our choosing. Thus far, in order to calibrate the experimental equipment and offline analysis procedures, the measurements have involved stable nuclides with well-known cross sections. With the aim of firmly establishing nuclear physics measurements with high intensity lasers without recourse to large-scale accelerator or reactor facilities, the next step involves precise quantitative measurements of physical properties on radionuclides. A detailed procedure for such measurements has been developed at ITU. It will be put to the test around the middle of 2007, after the upgrade of the UHI-10 laser is complete.

Contact:

J. Magill, tel.: +49 7247 951 366
joseph.magill@ec.europa.eu

6.2 Partitioning

Aqueous reprocessing

The reduction of radiotoxicity in nuclear waste by transmutation relies on efficient recovery and recycling of Minor Actinides (MA) from PUREX raffinates. The European research over the last decade, i.e. in the NEWPART, PARTNEW and the recent EUROPART programs, has resulted in the development of the combination of DIAMEX and the SANEX processes [1]. These are based on the co-separation of trivalent actinides and lanthanides (DIAMEX) by a diamide followed by the subsequent selective separation of MA in the SANEX.

DIAMEX

Recent research has shown that the tridentate TODGA (N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamide) extractant, exhibits even higher affinity for trivalent actinides than the reference diamide and could therefore be an interesting alternative to the DIAMEX process. During this year MA reprocessing from a genuine spent fuel solution by the TODGA process has been demonstrated.

Two batch extraction tests were carried out with the TODGA extractant using the genuine HAR solution as feed. The purpose with the experiments was to investigate if the properties were suitable for the hot process test using centrifugal contactors. These experiments showed that the extraction of lanthanides, Am and Cm is very efficient, scrubbing and stripping are possible and stripping will be even better in a multistage section due to lower acidity. Based on the batch extraction tests and several previous spiked tests (performed in FZJ, Germany) in centrifugal contactors in combination with computer code calculations (CEA, Marcoule) an optimised 32 stage centrifugal counter-current flow-sheet was proposed (see Fig. 1). Transient samples from the effluents were

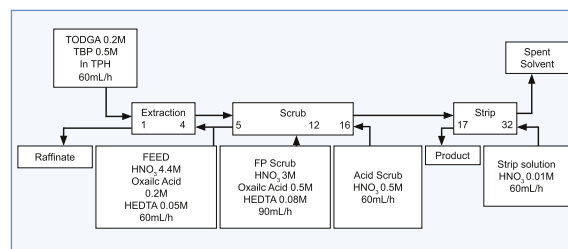


Fig. 1: Flow-sheet used for the hot TODGA test

collected at different time intervals during the experiment in order to follow the concentration build-up in the outgoing solutions. All aqueous samples were analysed by ICPMS and organic samples by gamma spectroscopy. The acidity profile was determined for the aqueous phase by titration with NaOH. In addition modelling of all profiles including concentration build-up curves has been carried out. The extraction of the Am and Cm were very efficient yielding more than 95% recovery in the product fraction.

SANEX

In order to overcome the drawbacks arising when using the BTP molecule as extractant for the SANEX process, i.e. difficulties in backextraction due to a strong bond between the An and ligand, University of Reading has developed a new family of ligands, BTBP.

Two batch experiments were carried out with the CyMe4-BTBP(6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2']-bipyridine) extractant using a DIAMEX product (An/Ln) solution as feed. The tests show that CyMe4-BTBP is a promising candidate for a demonstration test of the SANEX process. A centrifugal test is planned to be carried out during 2007 in collaboration with FZJ (Forschungszentrum Jülich).

[1] B. Christiansen et al., *Radiochim. Acta* 92 (2004) 475

Contact:

B. Christiansen, tel.: +49 7247 951 328
birgit.christiansen@ec.europa.eu

Pyrochemical reprocessing

Pyro-partitioning of actinide elements from high level liquid waste

In collaboration with CRIEPI (Japan) pyro-partitioning of actinides from fission products in a molten salt is being demonstrated. This process is based on the selective reductive extraction between the molten chloride salt solvent and a liquid metal phase. As input material a High Level Liquid Waste (HLLW) from PUREX reprocessing of irradiated UO₂ and MOX



Fig. 2: Calcinated high level liquid waste from PUREX reprocessing

fuels was used, having a concentration of 600 ppm of transuranium elements and 2000 ppm of fission products including 900 ppm of rare-earth elements. Roughly 500 ml of this solution was concentrated by evaporation in a glass vessel and calcined in a stainless steel crucible purged with air at 500 °C. Pre-experiments using simulated HLLW solutions had proven the applicability of stainless steel in this process. After 88 hours, 7.32g of calcined material could be collected (see Fig. 2). In the following steps, this material will be converted to chlorides in a graphite crucible under chlorine gas atmosphere. In the following reductive extraction step, the actinide elements in the chlorinated material will be selectively reduced to metal using metallic lithium as a reductant leaving most of the fission products in the salt phase.

Electrorefining of An from AnZr alloy fuels onto solid Al

An electrorefining process, in the molten chloride salts using solid aluminium cathodes to recover the actinides from their mixture with the lanthanides is being developed in ITU. The high capacity of aluminium to load the actinides by forming an An-Al alloy has been already shown as well as the selectivity of the process. Complete recovery of actinides by electrorefining of An-Zr alloy fuels can not be achieved without co-dissolution of Zr. It has been shown in previous experiments that the presence of Zr ions resulted in a significant deterioration in the quality of the deposit. For comparison Fig. 3 shows SEM micrographs of the deposit formed with and without the presence of Zr ions in the melt. The work has been focussed on

6. Partitioning and Transmutation

a better understanding of the electrochemical behaviour of Zr ions in LiCl-KCl melt and on the determination of the Zr distribution during the electrorefining process. In addition, UPuZr alloy electrorefining in a melt containing Zr ions at the beginning of the process has been demonstrated. It was shown that Zr^{4+} was completely chemically reduced by the addition of UPuZr alloy forming Zr particles in the melt. The electrorefining process yielded compact deposits consisting of UAl_3 , UAl_4 , $PuAl_3$ and $PuAl_4$ alloys with almost 100 % current efficiency.

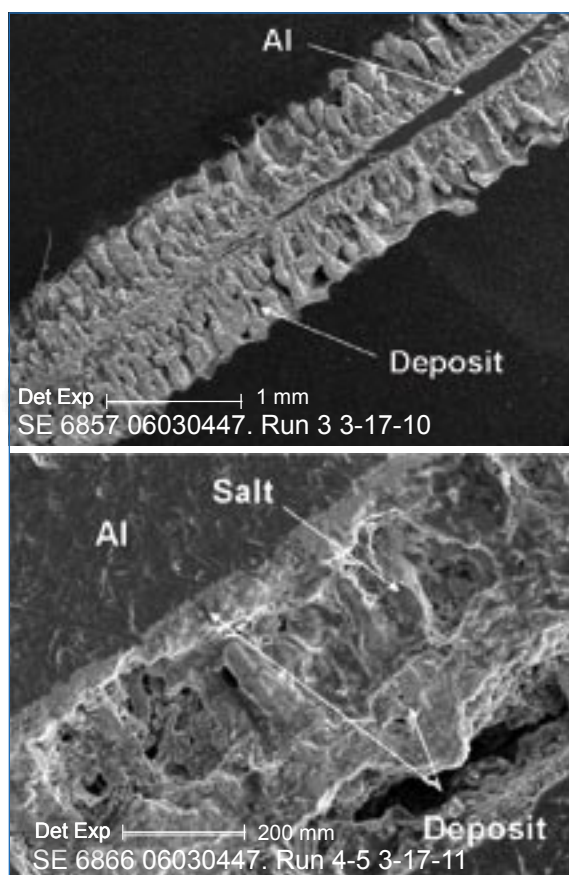


Fig. 3: SEM micrographs of Al electrodes with deposits consisting of U-Pu-Al alloys prepared without (left) and with (right) the presence of Zr ions in the melt

Contact:

R. Malmbeck, tel.: +49 7247 951 376
rikard.malmbeck@ec.europa.eu

6.3 Conditioning

Investigation of ceramics for the immobilization of actinides

Various phosphate, titanate and zirconate based ceramics are envisioned as potential host for transuranium elements immobilization. In 2006 the work was primarily focussed on phosphate materials, of monazite- and cheralite-type, $A^III PO_4$ and $B^II C^IV (PO_4)_2$ respectively ($A = Ln, An$; $B = Ca, Ba, Sr, Pb$; $C = An, Ti, Zr, Hf, Sn, Ge$). Those compounds are attractive for the immobilization of actinides because they can form solid solutions with the general formula $A^III_{2-2x} B^II_x C^IV_x (PO_4)_2$ which gives them more flexibility in terms of incorporation of actinides with different oxidation states and cationic radius. Various compositions have been synthesised and their crystal structure and thermodynamic properties investigated. The $CaTh(PO_4)_2$ compound was obtained by solid state reaction and low-temperature heat capacity measurements performed in the range $T = (0.5 \text{ to } 300) \text{ K}$. Enthalpy increments were determined from $T = (485 \text{ to } 1565) \text{ K}$. The $BaM^IV(PO_4)_2$ ($M = An, Ln, Ti, Zr, Hf, Sn, Ge$) compounds were also extensively investigated. Such phosphates containing a tetravalent cation with a radius smaller than 0.72 \AA ($CN=VI$) crystallize in the monoclinic $C2/m$ space group. XRD, SEM, DTA-TG and XPS analysis suggest that " $BaCe(PO_4)_2$ " (previously reported in the literature and indexed in the $P2_1/n$ space group) do not form because Ce^{IV} is reduced to Ce^{III} which can also be expected for Pu, Am and Cm. Only $BaTh(PO_4)_2$ phosphate crystallises in the $P2_1/n$, and thus can form solid solutions with $M^III PO_4$ monazites.

Other materials are also under investigation such as pyrochlore, zirconolite and thorium-phosphate-diphosphate (TPD) compounds. These studies are performed in collaboration with various academic and research institutions such as the universities of Manchester (UK), Münster (Germany) and Orsay (France).

References

- K. Popa et al., *Thermochim. Acta* 450 (2006) 1-4
- T. Geisler et al., *J. Sol. State Chem.* 179 (2006) 1489

Contact:

P. Raison, tel.: +49 7247 951 806
philippe.raison@ec.europa.eu

Selected Publications

- H. Schwoerer, J. Magill, B. Beleites (Eds.)
Lecture Notes in Physics: Lasers and Nuclei Applications of
Ultrahigh Intensity Laser in Nuclear Science, Springer (2006)
- B. Christiansen, C. Apostolidis, R. Carlos, O. Courson, J.-P. Glatz,
R. Malmbeck, G. Pagliosa, K. Römer, D. Serrano-Purroy
Advanced aqueous reprocessing in P&T strategies: process
demonstrations on genuine fuels and targets.
Radiochim. Acta 92 (2004) 475
- D. Haas, A. Fernandez, C. Naestren, D. Staicu, J. Somers,
W. Maschek, X. Chen
Properties of cermet fuels for minor actinides transmutation in
ADS.
Energ. Convers. Manag. 47 (2006) 2724
- K. Popa, R.J.M. Konings, O. Benes, T. Geisler, A.F. Popa
Thermodynamic and spectroscopic studies on the phase transition
of BaHf(PO₄)₂.
Thermochim. Acta 451 (2006) 1-4

Collaborations

- Belgium:** V. Sobolev (Studiecentrum voor
Kernenergie/Centre d'Étude de l'Énergie
Nucléaire SCK/CEN, Mol)
- Czech Republic:** M. Hron, J. Uhlir (NRI, Rež)
- France:** M. A. Kellett (Nuclear Energy Agency –
Organization for Economic
Co-operation and Development NEA-
OECD); J. Tommasi, G. Youinou,
F. Delage, S. Pilon, J.M. Bonnerot
(Commissariat à l'Énergie Atomique
CEA Cadarache); P. Baron, C. Madic,
C. Renault, D. Warin (CEA Saclay);

C. Garzenne (Électricité de France EDF)
- Germany:** R. Fromknecht (Forschungszentrum
Karlsruhe FZK-IFP); T. Geisler-
Wierwille (Univ. Münster);
W. Maschek (Forschungszentrum
Karlsruhe FZK); G. Modolo
(Forschungszentrum Jülich FZJ)
- Italy:** M. Fernando, P. Marucci (Ente per
le Nuove Tecnologie, l'Energia e
l'Ambiente ENEA, Rom)
- Japan:** T. Ogawa (Japan Atomic Energy
Research Institute JAERI), T. Inoue
(Central Research Institute of the
Electric Power Industry CRIEP);
S. Yamanaka (Univ. Osaka)

- Netherlands:** R.P.C. Schram, F. Klaassen (NRG,
Petten); F. Scaffidi-Argentina (Joint
Research Centre JRC-IE, Petten)
- Russia:** A. I. Orlova (Nizhegorosky State Univ.)
- Sweden:** J. Wallenius (KTH, Stockholm),
J. Kierkegaard (Studsvik Nuclear),
C. Ekberg (Chalmers Univ.)
- Switzerland:** C. Degueldre, F. Ingold (Paul Scherrer
Institut PSI, Villingen)
- UK:** K.W.D. Ledingham, P. McKenna (Univ.
Strathclyde); P. A. Norreys (Rutherford
Appleton Laboratory); T. Abram
(British Nuclear Fuel plc BNFL);
R. Thetford (Nexia Solution, Risley)
- USA:** W. Weber (PNL, Richland)

7. Alpha-Immunotherapy / Radiobiology

Highlight

Expanding Alpha-Immunotherapy Towards Therapy of Fungal, Bacterial and HIV Infections

Collaboration between ITU and Albert Einstein College of Medicine, New York

After nearly 20 years of development Alpha-immunotherapy (AIT) is now widely accepted as a promising strategy for the treatment of a variety of cancers and has moved from the pre-clinical stage into the clinical phase. Worldwide clinical trials are ongoing for the treatment of leukemia and malignant melanoma, and the treatment of brain tumour patients is planned to be continued in 2007. While continuing to develop the application of AIT in cancer therapy, ITU is also supporting novel concepts to expand the use of alpha emitters into new fields. In a joint project between ITU and the group of E. Dadachova at Albert Einstein College of Medicine (AECM) in New York, a variety of entirely new applications of alpha emitters in nuclear medicine have been pioneered. The main focus of collaboration lies on the therapy of fungal, bacterial and viral infections with particular relevance for patients with impaired immune system, where conventional treatments are not effective or simply do not exist. In 2006 the results of three important studies in that field were published: a fundamental study on the principles of interaction of radiolabelled antibodies with fungal cells [1], the first report on the successful targeting on fungal biofilms [2], and the first report on selective targeting and effective killing of HIV infected cells *in vitro* and *in vivo* [3].

In the Journal of Infectious Diseases, E. Dadachova et al. report on the mechanisms of interaction of radiolabelled antibodies with fungal cells and components of the immune system [1]. Although the same group had demonstrated earlier that AIT is effective against several fungal and bacterial infections [4-5], the underlying radiobiological mechanisms had remained uncertain. In this study the monoclonal antibody 18B7 that specifically binds to cells of the fungus *Cryptococcus neoformans* was labelled with ^{213}Bi , and its microbicidal effect was investigated *in vitro* and *in vivo*. It could be demonstrated that targeted alpha radiation from ^{213}Bi kills fungal cells and infected cells through various mechanisms, predominantly through direct hits with some contribution from the crossfire effect (see Fig. 1).

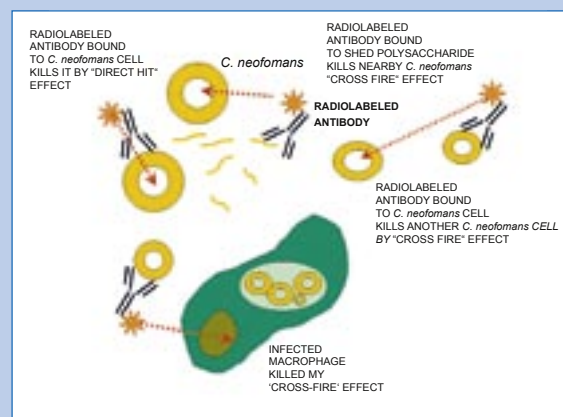


Fig. 1: Radiolabelled antibodies can kill fungal cells and infected cells through various mechanisms. "Direct hit" effects are predominant, with some contribution of cross-fire effect (from [1]).

In [2] Martinez et al. reported for the first time the use of microbe-specific monoclonal antibodies as delivery vehicles for the targeting of biofilms with cytotoxic radiation. Caused by infections, fungal biofilms can form on devices that are implanted into the human body, such as pacemakers, prosthetic joints and catheters. This is of growing concern as the rate of infection of these indwelling devices is relatively high, treatment often requires surgical intervention combined with antimicrobial therapy and biofilms on indwelling devices are often resistant to conventional antimicrobial agents. The high cell killing efficacy of alpha radiation can provide a new treatment option if the radiation can be selectively targeted to biofilms. Using confocal microscopy it could be demonstrated that the binding of the monoclonal antibody 18B7 is specific for *C. neoformans* biofilms, and it was also found that treatment with ^{213}Bi labelled 18B7 significantly reduced their metabolic activity. The results indicate that fungal biofilms are susceptible to treatment with targeted alpha radiation and suggest a novel option for the prevention or treatment of microbial biofilms on indwelling medical devices.

One of the main aspects of the collaboration between ITU and AECM has been to investigate the feasibility of targeting and destroying HIV infected cells using ^{213}Bi labelled carrier molecules. In November 2006 the first report of radiotherapy of HIV infections could be jointly published in PLoS Medicine [3].

In a person infected with HIV, the symptoms of AIDS can be delayed or controlled with drug combinations such as highly active antiretroviral therapy (HAART). However, at the moment there is no cure for HIV infection or AIDS. Even in people for whom HAART is successfully controlling disease, HIV remains at very low levels in white blood cells, and is capable of infecting more cells if treatment is stopped for some reason or becomes ineffective because the virus has developed resistance. One possible approach that could potentially eradicate HIV in an infected person is to inject radiolabelled antibodies, targeting HIV infected cells.

The *in vitro* studies demonstrated that it is possible to selectively target HIV-infected white blood cells using antibodies that bind to antigens displayed at the surface of infected cells. If these specific antibodies were labelled with ^{213}Bi the HIV infected cells could be efficiently destroyed (see Fig. 2). For *in vivo* studies mice were infected with HIV and treated with ^{213}Bi or ^{188}Re labelled antibodies. It was found that the number of HIV-infected cells in the treated mice was drastically reduced in a dose dependent manner

while toxicity was low. These results provide the first support for the idea that radio-immunotherapy might be an approach for treatment of HIV. It will be critical to find out whether the radioactively labelled antibodies are also safe and effective in humans.

References

- [1] E. Dadachova et al., J. Inf. Dis. 193 (10) (2006) 1427
- [2] L.R. Martinez et al., Antimicrob. Agents Chemother. 50(6) (2006) 2132
- [3] E. Dadachova et al., PLoS Med 3 (11) (2006) e427
- [4] E. Dadachova et al., Antimicrob. Agents Chemother. 48(5) (2004) 1624
- [5] E. Dadachova et al., Antimicrob. Agents Chemother. 48(3) (2004) 1004

Contact:

C. Apostolidis, tel.: +49 7247 951 389
christos.apostolidis@ec.europa.eu

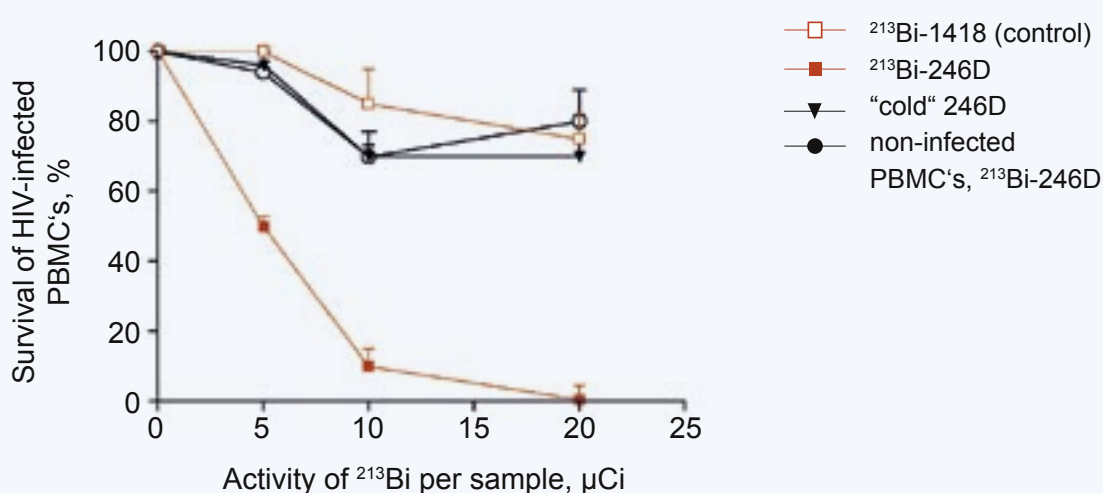


Fig. 2: Highly specific and effective *in vitro* killing of HIV-infected human Peripheral Blood Mononuclear Cells (PBMCs) with ^{213}Bi labelled human monoclonal antibodies. Target selective ^{213}Bi labelled antibody 246D leads to dose dependent cell kill (red full squares), while unlabelled "cold" antibody (black triangles) and ^{213}Bi labelled unspecific antibody (red open squares) show no effect. Non-infected PBMCs representing healthy cells are not affected by ^{213}Bi -246D (black circles) (from [3]).

7. Alpha-Immunotherapy / Radiobiology

The alpha-immunotherapy action has continued to contribute to the development and application of targeted alpha therapy (TAT) for the treatment of cancer and infectious diseases. The support of pre-clinical studies and clinical trials included the production of $^{225}\text{Ac}/^{213}\text{Bi}$ radionuclide generators and the provision of training, equipment and radiochemical support for hospitals. The treatment of melanoma patients at St. George Hospital in Sydney in the frame of a phase I clinical trial, and the first report on the successful targeting and killing of HIV-infected cells using ^{213}Bi in an animal model were two important achievements in 2006. Fundamental radiobiological studies in cooperation with the University of Düsseldorf led to the identification of time- and dose-dependent patterns of alpha-induced effects in a human lymphoma cell line at transcriptional level, accompanied by the functional characterization of irradiated cells.

7.1 Production of $^{225}\text{Ac}/^{213}\text{Bi}$ for Targeted Alpha Therapy

The production of $^{225}\text{Ac}/^{213}\text{Bi}$ from ^{229}Th remains an important activity within the Alpha-immunotherapy action. In 2006, 31 quality controlled $^{225}\text{Ac}/^{213}\text{Bi}$ shipments, corresponding to 0.4 Ci ^{225}Ac in total were provided to our various partners in Europe, USA and Australia. An overview of ITU's current collaborations in the field of TAT is given in Table 1. In order to ensure the safe and reliable use of the ITU standard generator in hospitals, its production and performance is continuously controlled and optimised. Using the ITU designed loading procedure from 4 M nitric acid the ^{225}Ac activity is distributed over two thirds of the generator resin as shown in Fig. 1.

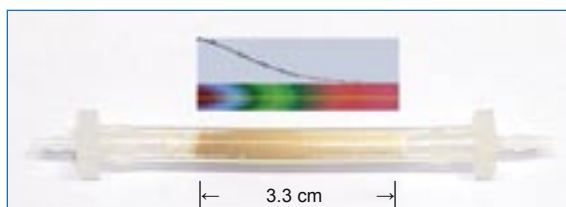


Fig. 1: The ITU standard $^{225}\text{Ac}/^{213}\text{Bi}$ radionuclide generator. The superimposed radiographic image shows the distribution of ^{225}Ac over approx. two thirds of the generator resin, reducing radiolytic degradation and increasing generator life-time.

In this manner the radiolytic degradation of the resin can be significantly minimized and the performance of the generator is stabilized over several weeks. An example of generator performance testing is shown in Fig. 2. The standard generator was eluted 52 times within 4 weeks with an average yield of ^{213}Bi of $76 \pm 3\%$ and low breakthrough of ^{225}Ac of 59 ± 60 ppb.

Partner	Cancer type or collaboration project
Technical University Munich, Department of Nuclear Medicine (D)	Gastric, ovarian and bladder cancer
University Hospital Düsseldorf (D)	Non-Hodgkin's lymphoma (NHL)
University Hospital Ulm (D)	Acute myeloid leukemia
INSERM, Nantes (F)	Multiple myeloma
University Hospital Basel (CH)	Brain tumors, prostate cancer
St. George Hospital & Centre for Experimental Radiation Oncology, Sydney (Australia)	Malignant melanoma, prostate, pancreatic, breast and ovarian cancer
Albert Einstein College of Medicine, New York (USA)	Fungal, bacterial and viral (HIV) infections
Johns Hopkins School of Medicine, Baltimore (USA)	Breast Cancer

Tab. 1

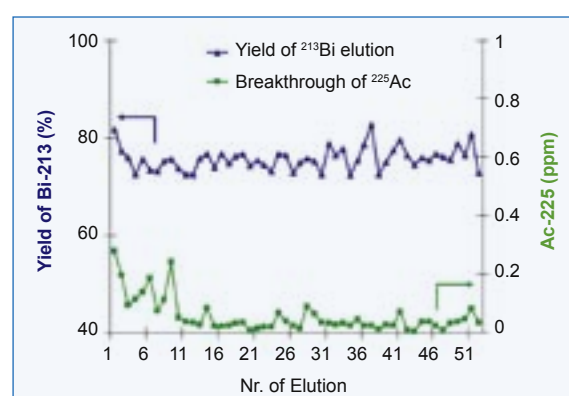


Fig. 2: Routine testing of an ITU standard $^{225}\text{Ac}/^{213}\text{Bi}$ generator. The generator showed constant yield of ^{213}Bi ($76 \pm 3\%$) and low breakthrough of ^{225}Ac (59 ± 60 ppb) over several weeks (52 elutions).

7. 2 Pre-clinical and Clinical Studies Supported by ITU

In the framework of collaborations with hospitals and cancer research centres, ITU has continued to support pre-clinical and clinical studies by providing radionuclides, training and know-how and specific equipment necessary for the handling of alpha-emitters. In 2006, pre-clinical studies in the field of gastric, ovarian, bladder, prostate, pancreatic and breast cancer, multiple myeloma and leukemia as well as a clinical study on malignant melanoma were supported. In the field of application of TAT for the treatment of infectious diseases, a joint project on the treatment of fungal, bacterial and viral (HIV) infections was continued (see *Highlight in this section*).

In a joint project with the Department of Nuclear Medicine of the Technical University of Munich, pre-clinical studies on gastric, ovarian and bladder cancer were continued. It had been shown previously that the gastric cancer cells HSC45-M2 can be specifically targeted by the monoclonal antibody d9MAb coupled to the alpha emitter ^{213}Bi . Mouse studies showed that therapy with ^{213}Bi -d9MAb immunoconjugates effectively kills tumour cells and leads to significant prolongation of survival. Recently a bioluminescence method for improved *in vivo* imaging of tumour growth and treatment response could be established through transfection of gastric cancer cells with firefly luciferase [1]. The method is illustrated in Fig. 3 showing bioluminescence images of a mouse at various times after tumour cell inoculation and ^{213}Bi -d9MAb therapy. In the field of ovarian cancer *in vitro* binding studies showed that ^{213}Bi -anti-EpCam immunoconjugates exhibit excellent binding to the ovarian cancer cell lines OV-MZ-10 and OV-MZ-15. Consequently a peritoneal carcinomatosis model will be established to study the therapeutic efficacy of ^{213}Bi -anti-EpCam. Investigation of thera-

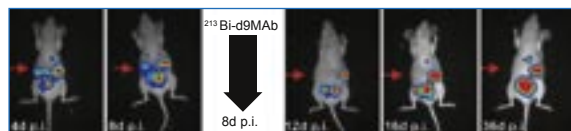


Fig. 3: Bioluminescence images of a mouse at 4, 8, 12, 16, and 36 days post inoculation (d p.i.) with gastric cancer cells transfected with firefly luciferase. Images on day 4 and 8 show tumour establishment and growth. Following ^{213}Bi -d9MAb therapy on day 8, tumour response can be monitored. Elimination of small tumour nodules is marked by red arrows (from [1]).

peutic efficacy of ^{213}Bi -anti-EGFR conjugates for the treatment of bladder cancer is underway. Treatment response will be monitored using the newly established bioluminescence imaging method.

In collaboration with the University Hospital Basel, a pre-clinical study on the therapy of prostate cancer using ^{213}Bi -labelled peptides was started. Low-molecular peptides are ideal carrier molecules in combination with relatively short-lived ^{213}Bi ($T_{1/2} = 46$ min) due to their relatively fast diffusion and rapid tumour targeting. Bio-distribution studies of ^{213}Bi -DOTA-PESIN in a mouse model of prostate cancer demonstrated a high tumour uptake of 11% ID/g already 1 hour after injection. Therapeutic studies

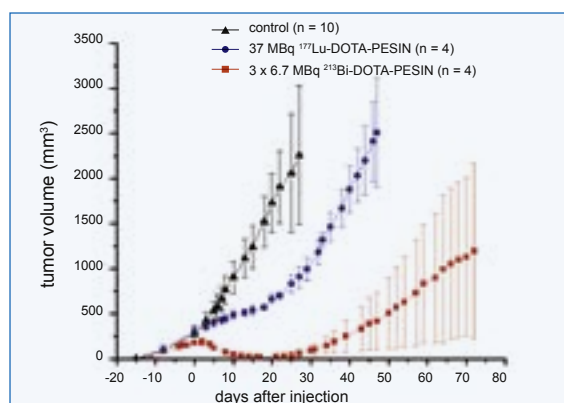


Fig. 4: Therapeutic efficacy of DOTA-PESIN labelled with the alpha emitter ^{213}Bi or the low energy beta emitter ^{177}Lu in a prostate cancer mouse model. While the application of 37 MBq of ^{177}Lu -DOTA-PESIN could not control tumour growth, 20 MBq ^{213}Bi -DOTA-PESIN led to near complete tumour regression. Two step treatment regimes with a second ^{213}Bi -DOTA-PESIN injection at day 21 are currently under study to prevent tumour re-growth.

comparing the efficacy of DOTA-PESIN labelled with ^{213}Bi and the low energy beta emitter ^{177}Lu showed the superiority of the alpha emitter (see Fig. 4). The application of 20 MBq ^{213}Bi -DOTA-PESIN 11 days after tumour inoculation resulted in near complete tumour regression, while 37 MBq of ^{177}Lu -DOTA-PESIN could not control tumour growth. Currently 2-step treatment regimes using ^{213}Bi -labelled peptides are under study to eradicate residual tumour cells and prevent tumour re-growth.

The treatment of metastatic breast cancer using ^{213}Bi -labelled monoclonal antibody 7.16.4 is under investigation in a joint project with Johns Hopkins School of Medicine in Baltimore, USA.

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A mouse model of breast cancer metastases was successfully set up and establishment and progression of metastases in multiple organs, including bones, liver and spleen were confirmed by *in vivo* animal imaging and histopathology. The maximum tolerated dose (MTD) was found to be 120 μCi (40 $\mu\text{Ci}/\text{day}$ for 3 consecutive days) that allowed 100% survival of mice with no significant (>15%) body weight loss. To evaluate therapeutic efficacy of ^{213}Bi -7.16.4, three days after tumour cell inoculation mice were treated with (a) ^{213}Bi -7.16.4 with a total dose of 120 μCi ; (b) ^{213}Bi -Rituxan (non-specific control) with a total dose of 120 μCi ; or (c) no treatment control. Significant improvement in time of survival has been found for the group that received 120 μCi ^{213}Bi -7.16.4 with a median survival time of 41 days compared to 28 days for the untreated controls (see Fig 5). The studies demonstrate that ^{213}Bi labelled monoclonal antibody 7.16.4 is effective in treating early stage breast cancer micrometastases without severe toxicity to cross reactive normal organs.

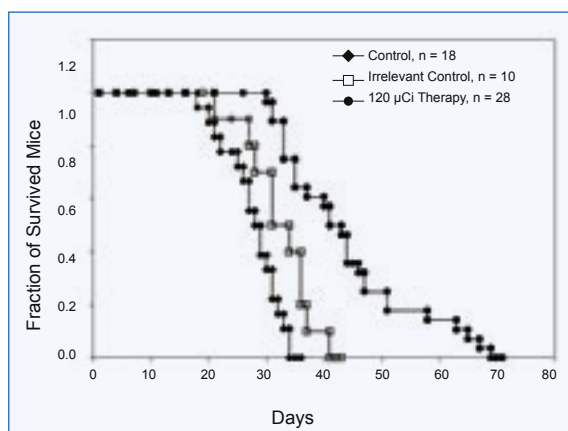


Fig. 5: Survival curves in a mouse model of breast cancer metastases. Mice treated with 120 μCi ^{213}Bi -7.16.4 showed a significantly prolonged survival compared to untreated controls and mice treated with ^{213}Bi -labelled unspecific antibody.

TAT of multiple myeloma using ^{213}Bi -labelled monoclonal antibody BB4 is under study at INSERM, Nantes in collaboration with ITU. The main goal of the joint project is to investigate whether combining TAT and chemotherapeutic drugs (paclitaxel, doxorubicin, dexamethasone or vinblastine) leads to synergistic effects. *In vitro* studies demonstrated that paclitaxel was highly synergistic with TAT and doxorubicin was additive or moderately synergistic, depending on incubation time. Dexamethasone and TAT showed an

additive effect, vinblastine did not improve the efficacy of TAT (infra-additive or additive combination). These results suggest that the combination of TAT with paclitaxel or doxorubicin should be explored further in clinical trials assessing the treatment of multiple myeloma or in the conditioning regimens delivered prior to autologous bone marrow transplantation.

The collaboration between ITU and the Centre of Experimental Radiation Oncology at St. George Hospital in Sydney has continued to be very active. Pre-clinical studies on prostate, pancreatic and ovarian cancer were conducted and a phase I clinical trial on ^{213}Bi therapy of malignant melanoma was continued. In the

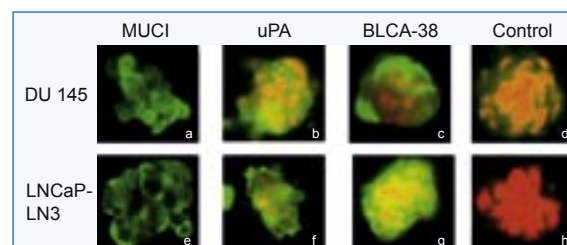


Fig. 6: Targeting of prostate cancer cell spheroids (DU 145 and LNCaP-LN3) by two monoclonal antibodies (c595 and BLCA-38) and the peptide PAI2. Green immunofluorescence staining indicates positive cells. All photographs $\times 20$ original magnification. The MUC1 antigen targeted by c595 is detected in DU 145 (a) and LNCaP-LN3 (e) spheroids. uPA is the target for PAI2 and is expressed weakly in DU 145 spheroids (b) but moderately in LNCaP-LN3 spheroids (f). BLCA-38 MAb is weakly positive for DU 145 spheroids (c) but strongly positive for LNCaP-LN3 spheroids (g). No staining is found in control DU 145 (d) and LNCaP-LN3 (h) spheroids (from [3]).

field of prostate cancer the therapeutic efficacy of the ^{213}Bi -labelled peptide PAI2 could be demonstrated in a mouse xenograft model of PC3 cells. Single and multiple dose TAT was highly effective within tolerance limits and led to significant retardation or complete inhibition of tumour growth depending on the time interval between tumour cell inoculation and treatment [2]. To further improve the targeting of prostate cancer *in vivo* by overcoming the heterogeneous expression of targeted antigens, a multiple targeting approach using a mixture of two monoclonal antibodies and the peptide PAI2 as carrier molecules was developed as illustrated in Fig. 6 [3]. PAI2 labelled with ^{213}Bi was shown to be also effective and safe in the therapy of micrometastatic pancreatic cancer in a mouse model [4]. The excellent pre-clinical results led to the initiation of a clinical phase I study planned to begin in

2007 at Royal North Shore Hospital in Sydney. The cytotoxicity of PAI2 as well as the monoclonal antibodies c595 and Herceptin labelled with ^{213}Bi was studied in ovarian cancer cell monolayers and clusters. Out of the three tested immunoconjugates, ^{213}Bi -PAI2 and ^{213}Bi -c595 were found to be highly cytotoxic to ovarian cancer cells and are potential candidates for the control of ovarian cancer at the minimal residual disease stage [5]. Within a phase I dose escalation study 27 patients with stage IV melanoma/ in-transit metastasis have been treated to date using ^{213}Bi -labelled monoclonal antibody 9.2.27. At the relatively low dose levels administered at this stage of the study 50% of patients showed stable disease and 12% showed partial response. The study is continued in 2007.

Contact:

A. Morgenstern, tel.: +49 7247 951 248
alfred.morgenstern@ec.europa.eu

7. 3 Radiobiological Studies

Understanding radiation therapy requires information on the mechanisms underlying the cytotoxic effects of radiation. To date, little evidence has been obtained for the molecular lesions induced by alpha-immunoconjugates. The aim of the radiobiology programme of ITU is to generate a „molecular portrait“ of the alpha radiation-induced effects in human cells. During radiation exposure, structured energy deposition patterns interact on multiple scales with the biological structures and produce correlated damage. For alpha particles, high ionization densities occur along a linear track and DNA lesions induced are less repairable than those created by more sparsely ionizing radiation. The special features that characterize the biologic effects consequent to the traversal of charged particles through human normal and cancer cells were explored with respect to DNA lesions and cellular responses.

In collaboration with the University of Düsseldorf and in frame of a project supported by the German Ministry for Education and Research (Bundesministerium für Bildung und Forschung, BMBF), the study of the mechanisms of cytotoxicity induced by targeted alpha irradiation in human normal and malignant he-

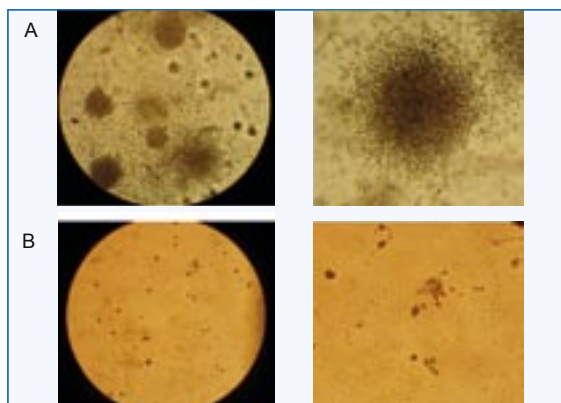


Fig. 7: Tumour cell colonies of K422 lymphoma cells as grown after two weeks of culture in a semisolid methyl-cellulose medium (optical microscope, magnification: left, 50x; right, detail).

A – unirradiated control cells. The colony-forming ability is a criterion for reproductive integrity of cells.

B – cells treated with 100 μCi ^{213}Bi -CD20 for 46 min. The drastic reduction of colony size and the failure to form colonies indicate loss of reproductive integrity at early post-irradiation divisions.

matopoietic (blood-forming) cells was continued. Human lymphoma cells treated with different activity levels of ^{213}Bi -CD20 have been examined after various irradiation periods with respect to survival, proliferation, ability to form tumour cell colonies (clonogenicity), cell death (apoptosis/necrosis) and DNA alterations (double strand breaks, methylation). The first results showed that alpha exposure influenced cell proliferation in a time-dependent manner and induced an arrest in the G2-phase of the cell cycle. Alpha-induced DNA double strand breaks have been visualized and despite the high initial cell survival rate (about 90% after 24 h of irradiation), irradiated cells completely lost their clonogenic capacity: no colonies could be detected two weeks after irradiation (see Fig. 7).

These results indicate the profound alpha-induced damage, which rendered clonogenic cancer cells incapable of multiplication and growth and suggest that initial hits are responsible for death of target cells or their off-springs [6]. Considering the alpha-induced cell death, it was interesting to observe its occurrence by pathways different from apoptosis (programmed cell death), as stated before for radiation-induced cell death.

To get a deeper insight into the molecular effects of alpha irradiation and in an attempt to get a more com-

7. Alpha-Immunotherapy / Radiobiology

prehensive view of the cellular responses, the gene expression profiles of the irradiated cells were identified. The “expression profile” or “transcriptome” of the cell represents the collection of genes that are expressed or transcribed from DNA into RNA and reflects the exact functional state of a cell at a certain moment. As it also shows the relationship between the genes involved, this type of integrative approach could increase the understanding of the radiation response at molecular level. To this aim, the previously used cDNA Clontech arrays were replaced by the Affymetrix technology, which allows a broader screening of the molecular changes contributing to the overall cellular radiation response by examining about 8,700 genes at once [7]. The considerable amount of resulting data requires an important bioinformatical support for processing and analysis. The bioinformatic analysis of Affymetrix-Chips data including normalization, permutation tests, hierarchical cluster analysis, pathway-software-programs has been refined and successfully applied to 112 samples of normal and malignant hematopoietic cells. The systematic data assessment revealed three different time-dependent patterns of changes in gene expression after alpha exposure of K422 lymphoma cells: 1. early up-regulation, as early as after one hour of irradiation (76 genes); 2. late up-regulation at 24 hours of irradiation (394 genes); 3. down-regulation (11 genes). By using different gene banks, differentially expressed genes were divided into functional families, according to their biological function. The identified major functional groups are as follows: cell cycle (52 genes), immune response (48 genes), transcription regulation (40 genes), DNA replication (28 genes) and DNA repair (22 genes), RNA processing (19 genes), proteolysis (13 genes). An interim interpretation of the results suggests that alpha irradiation preferentially induces transcription factors, influences cell cycle regulation and switches on DNA repair mechanisms. An interesting finding is the up-regulation of B-cell genes involved in the immune response. On the background of the expression data, isolated genes have been selected for confirmation by using different methods, on protein or mRNA level and, as shown before, the analysis has been correlated with functional tests. Summarizing, gene expression analysis under consideration of bioinformatic algorithms allowed to identify the influence of targeted alpha irradiation at the level of gene transcription and made it possible to assess significant gene expression differences between normal blood lymphocytes and K422 lymphoma cells.

Another topic was the comparison of alpha versus beta radiation-induced effects at transcriptional level. In an experimental design using the same target cells (human K422 lymphoma cells) and the same carrier for the radioactive isotope (anti-CD20 monoclonal antibody), equal activities of ^{213}Bi and ^{90}Y were compared. In contrast to beta particles which have a low linear energy transfer (LET, $0.2 \text{ keV}/\mu\text{m}$) and a long range of up to several mm in human tissues, alpha particles have a 500-fold higher LET ($100 \text{ keV}/\mu\text{m}$) and a short range of only a few cell diameters (40 to $80 \mu\text{m}$). As a result, the energy of alpha-particles is mainly delivered to the target cells while sparing healthy surrounding cells. The high LET of alpha particles provides a correspondingly greater biological impact when compared with an equivalent number of cellular traversals by lower LET beta particles. The preliminary gene expression data confirmed these differences. An alpha-induced gene expression profile and a beta-induced gene expression profile were found, which are clearly distinct. The response to targeted alpha radiation was greater with respect to the number of genes altered and the functional categories the genes belong to. This indicates the specificity of cellular reaction in response to radiation exposure as a function of track structure or ionization density.

The increasing use of ^{213}Bi as a tool for treating disseminated cancers prompted the detailed exploration of targeted alpha-immunotherapy for solid tumours. For the *in vitro* study of these entities, a culture of

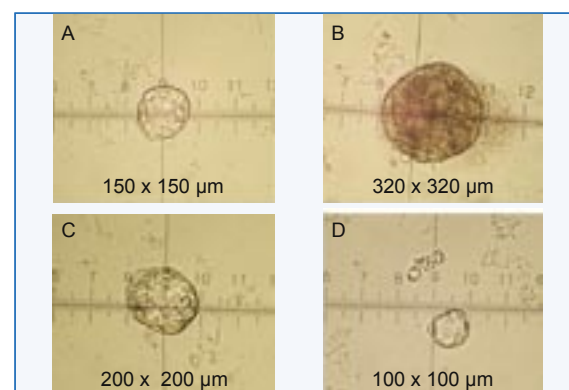


Fig. 8: Breast cancer spheroids (MCF-7 cells). The optical microscope images show the size differences between control (unirradiated) spheroids and spheroids treated with two different doses of ^{213}Bi -Herceptin after 3 weeks growth in culture (A: spheroid before treatment, B: untreated control spheroid after 3 weeks, C: 0.6 MBq/ml ^{213}Bi -Herceptin, D: 1.2 MBq/ml ^{213}Bi -Herceptin). Herceptin is a monoclonal antibody which specifically recognizes breast cancer cells.

breast cancer spheroids, which resemble microscopic tumours was established. These allowed the assessment of the growth-inhibiting effects of specifically targeted alpha emitters in dependency of dose and incubation time (see Fig. 8).

The molecular data on the biological effects of alpha irradiation and further of the genetic determinants of radiosensitivity may provide not only the means of a better patient selection, but also a basis for optimized dose concepts and treatment schedules.

References

- [1] M. Buchhorn et al., Eur J Nucl Med Mol Imaging (2007) DOI: 10.1007/s00259-006-0311-3
- [2] S. Rizvi et al., Cancer Biol. Ther. 5 (2006) 386
- [3] J. Wang et al., Prostate 66 (2006) 1753
- [4] C. F. Qu et al., Clin. Exp. Metastas. 22 (2005) 575
- [5] Y. J. Song et al., Cancer Lett. 234 (2006) 176
- [6] S. Martin et al., J Nucl Med 47(suppl 1) (2006) 627
- [7] S. Raschke et al., Onkologie 29 (suppl 3) (2006) 159

Contact:

S. Martin, tel.: +49 7247 951 224
simona.martin@ec.europa.eu

Selected Publications

- E. Dadachova, R. A. Bryan, C. Apostolidis, A. Morgenstern, T. Zhang, T. Moadel, M. Torres, X. Huang, E. Revskaya, A. Casadevall
Interaction of radiolabeled antibodies with fungal cells and components of immune system in vitro and during radioimmunotherapy of experimental fungal infection.
J. Infectious Diseases 193 (2006) 427
- L. R. Martinez, R. A. Bryan, C. Apostolidis, A. Morgenstern, A. Casadevall, E. Dadachova
Antibody-guided alpha radiation effectively damages fungal biofilms.
Antimicrob. Agents Chemother. 50 (2006) 2132
- E. Dadachova, M. C. Patel, S. Toussi, C. Apostolidis, A. Morgenstern, M. W. Brechbiel, M. K. Gorny, S. Zolla-Pazner, A. Casadevall, H. Goldstein
Targeted killing of virally infected cells by radiolabeled antibodies to viral proteins.
PLoS Med 3(11) (2006) e427
- B. J. Allen, C. Raja, S. Rizvi, Y. Li, W. Tsui, P. Graham, J. F. Thompson, R. A. Reisfeld, J. Kearsley, A. Morgenstern, C. Apostolidis

- Intralesional targeted alpha therapy for metastatic melanoma.
Cancer Biol. Ther. 4(12) (2005) 1318
- S. A. Rizvi, Y. Li, E. Song, C. F. Qu, C. Raja, A. Morgenstern, C. Apostolidis, B. Allen
Preclinical studies of Bismuth-213 labeled plasminogen activator inhibitor type 2 (PAI2) in a prostate cancer nude mouse xenograft model.
Cancer Biol. Ther. 5(4) (2006) 386
- J. Wang, S. Rizvi, M. C. Madigan, P. J. Cozzi, C. A. Power, C. F. Qu, A. Morgenstern, C. Apostolidis, P. J. Russell, B. J. Allen, Y. Li
Control of prostate cancer spheroid growth using (213)Bi-labeled multiple targeted alpha radioimmunoconjugates.
Prostate 66 (16) (2006) 1753
- S. Kneifel, D. Cordier, S. Good, M. C. Ionescu, A. Ghaffari, S. Hofer, M. Kretzschmar, M. Tolnay, C. Apostolidis, B. Waser, M. Arnold, J. Mueller-Brand, H. R. Maecke, J. C. Reubi, A. Merlo
Local targeting of malignant gliomas by the diffusible peptidic vector 1,4,7,10-tetraazacyclododecane-1-glutaric acid-4,7,10-triacetic acid-substance p.
Clin. Cancer Res. 12(12) (2006) 3843
- K. Vandenbulcke, H. Thierens, F. D. Vos, J. Philippe, F. Offner, A. Janssens, C. Apostolidis, A. Morgenstern, K. Bacher, V. de Gelder, R. A. Dierckx, G. Slegers
In vitro screening for synergism of high-linear energy transfer (213)Bi-radiotherapy with other therapeutic agents for the treatment of B-cell chronic lymphocytic leukemia.
Cancer Biother. Radiopharm. 21(4) (2006) 364
- F. Neumann, S. Harmsen, S. Martin, R. Kronenwett, M. Kondakci, M. Aivado, U. Germing, R. Haas, G. Kobbe
Rituximab long-term maintenance therapy after autologous stem cell transplantation in patients with B-cell non-Hodgkin's lymphoma. Ann. Hematol. 85 (8) (2006) 530

Collaborations

- Australia:** B. Allen (St. George Cancer Care Center, Sydney)
- Austria:** R. Capote Noy (IAEA, Nuclear Data Section)
- Czech Republic:** O. Lebeda, J. Stursa (Nuclear Physics Institute, Rez)
- France:** M. Cherel, F. Davodeau (Institut National de la Santé et de la Recherche Médicale, Paris)
- Germany:** R. Haas, R. Kronenwett, S. Raschke (University Hospital Düsseldorf); R. Senekowitsch-Schmidtke, C. Seidl (Technical University Munich); S. Reske, B. Neumaier, C. Friesen (University Hospital Ulm)
- Italy:** K. Abbas, F. Simonelli (EC-JRC, Institute for Health and Consumer Protection, Ispra)
- Romania:** M. Sin (University of Bucharest)
- Switzerland:** H. Mäcke, S. Good, D. Wild (Kantonsspital Basel)
- USA:** E. Dadachova (Albert Einstein College of Medicine, New York); G. Sgouros (Johns Hopkins School of Medicine, Baltimore)

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List of Contributors to the Various Chapters

Basics

J.-F. Babelot, T. Fanghänel, G. Tamborini, C. Walther, G. Weber

Actions

- **Safeguards Research and Development** (K. Mayer / Action Leader)
K. Casteleyn, L. Duinslaeger, M. Hedberg,
K. Lützenkirchen, K. Mayer, H. Ottmar, A. Schubert, P. Van Belle, M. Wallenius, E. Zuleger
- **Measurement of Radioactivity in the Environment** (M. Betti / Action Leader)
L. Aldave de las Heras, M. Betti
- **Basic Actinide Research** (F. Wastin / Action Leader)
T. Gouder, R. Konings, J. Magill, F. Wastin
- **Spent Fuel Characterisation** (V.V.Rondinella / Action Leader)
C. Alecu, P. Carbol, J. Cobos-Sabate, D. Cui, J.P. Hiernaut, E. Kotomin,
R. Pehrman, V.V. Rondinella, D. Serrano-Purroy, P. Van Uffelen, D. Wegen, T. Wiss
- **Safety of Nuclear Fuels** (C.Walker / Action Leader)
D. Bottomley, S. Bremier, M. Ernstberger, H. Santa-Cruz, J. Somers,
J. Spino, D. Staicu, E. Toscano, P. Van Uffelen
- **Partitioning and Transmutation** (A. Fernandez-Carretero / Action Leader)
B. Christiansen, A. Fernandez-Carretero, J.P. Hiernaut,
J. Magill, R. Malmbeck, P. Raison, D. Staicu
- **Alpha-Immunotherapy / Radiobiology** (C. Apostolidis / Action Leader)
C. Apostolidis, S. Martin, A. Morgenstern

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European Commission

EUR 22669 EN - Institute for Transuranium Elements – Annual Report 2006

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Abstract

The annual report 2006 of the Institute for Transuranium Elements (ITU) of the Joint Research Centre describes the progress made during the fourth year of the 6th Framework Programme of the European Community for research, technological development and demonstration activities and of the 6th Framework Programme of the European Atomic Energy Community for research, training and activity.

In the first part of the report an overview with a summary of the scientific objectives, important events and facts & figures of ITU is given.

In the second part of the report, a more in-depth technical description of progress made in the seven actions is given, including highlight articles on important progress made during 2006.

Topics covered focus on:

Safeguards Research and Development

Review

Measurement of Radioactivity in the Environment

Mapping of Radionuclides in Biological Tissues by Secondary Ion Mass Spectrometry

Basic Actinide Research

Search for Higher Oxides of Pu - A Photoemission Study

Spent Fuel Characterisation

Effects of Alpha-decay Damage and Helium Accumulation in High Level Waste Forms

Safety of Nuclear Fuels

High Temperature Reactor Coated Particle Fuel

Partitioning and Transmutation

Thermal Properties of Cermets Fuels

Alpha-Immunotherapy / Radiobiology

Expanding Alpha-Immunotherapy Towards Therapy of Fungal, Bacterial and HIV Infections

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OUR MISSION

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